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THE UNIVERSITY OF ALBERTA

CYCLOBUTADIENE

by

Ⓒ FERNANDO A. SOUTO BACHILLER

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA
FALL, 1978

THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

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To Josefina

ABSTRACT

Cyclobutadiene (**1**) and its fully deuterated analogue (**28**) have been generated in rare gas matrices from several photoprecursors.

The infrared spectrum (Nicolet 7199 FT-IR Interferometer) of **1** isolated in an argon matrix exhibits absorptions at 1523 (w), 1240 (m), 723 (w), and 572 (s) cm^{-1} below 2000 cm^{-1}. The per-deuterio species **28** shows these bands shifted to 1456 (w), 1043 (m), 609 (m), and 421 (s) cm^{-1}. The following assignment of these observed bands to the normal modes of vibration of the molecule could be made. The band at 1523 cm^{-1} which shifts to 1456 cm^{-1} upon deuteration is undoubtedly due to the C=C stretching vibration of **1**. The absorption at 1240 cm^{-1} which shifts to 1043 cm^{-1} is largely due to the H-C-C in-plane bending vibration, and not primarily to the C-C stretching motion which contributes mainly to 723 cm^{-1}. In the per-deuterio species the bands at 1043 and 609 cm^{-1} are a mixture of these two coupled motions. The lines at 572 and 421 cm^{-1} are the sole out-of-plane hydrogen and deuterium bending vibrations.

These data are not consistent with an earlier conclusion that the molecule adopts a square conformation but instead indicate a rectangular geometry for the cyclobutadiene ring. The observed frequencies were

reproduced well through a GF normal coordinate calculation using a reasonable set of force constants. This calculation was kindly performed by Professor John E. Bertie of this Department.

Although the present study does not define the exact symmetry of the cyclobutadiene molecule, it provides a solution to the recent controversial cyclobutadiene problem. It is hoped that the findings described here lay the foundation for further developments in the chemistry of this molecule.

ACKNOWLEDGEMENTS

I wish to acknowledge personal debts of gratitude to my supervisor, Professor S. Masamune, for his patience, guidance, and continual encouragement.

It is a pleasure to acknowledge the help of the many people involved in creating the cryogenic system used during the course of this research. I am indebted to Messrs. Jack M. Ferch, Ernest N. Young, Leo Martyn, Theo Van Esch, and Fred Fitzgerald of the Machine Shop in this Department who built and assembled much of the equipment. Mr. Allan Clement provided valuable suggestions in the design of the spray-on gas line. Mr. Cornelius Brusselers and Mr. Gerald J. Streefkerk of the Glass Shop in this Department kindly assisted me in the fusing together of the many glass parts of the system.

Thanks are duly given to Mr. Robert N. Swindlehurst and his staff members in the Spectroscopy Laboratory for their invaluable services. The help of Mr. James Hoyle who greatly assisted me in the recording and plotting of the infrared spectra (Nicolet 7199 FT-IR Spectrophotometer) is gratefully acknowledged.

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Dr. K. Sakan for the synthesis of cyclobutenedicarboxylic anhydride-$\underline{d}_4$ and 12-oxa-tetracyclo[4.4.3.0.0^{2,5}]trideca-3,7,9-triene-2,3,4,5,7,8,9,10-$\underline{d}_8$; Dr. S. Ohta for the development of the route leading to the synthesis of α-pyrone-$\underline{d}_4$; Mr. James Diakur for a sample of phthalan; and Dr. R.L. Sobczak for his help in the preparation of 1,3-butadiene-$\underline{d}_6$. Last, but not least, I give special thanks to Dr. Margaret A. Armour who reduced my crude written versions of this thesis to an intelligible manuscript.

I express my gratitude to Ms Diane L. Dowhaniuk who made valuable suggestions in the final editing and kindly typed the manuscript.

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However, my greatest debt is to my wife, Josefina, who showed much patience and forbearence during the period in which I was performing the rather prolonged matrix experiments and who typed the rough draft of the manuscript.

Apologies

To all persons in this field whose work I have overlooked or misinterpreted.

For errors which the diligent will inevitably find in the text.

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"The chemists are a strange class of mortals impelled by an almost insane impulse to seek their pleasure among smoke and vapor, soot and flame, poison and poverty. Yet among these evils I seem to live so sweetly that may I die if I would change places with the Persian king."

J. J. BECHER (ca. 1675)

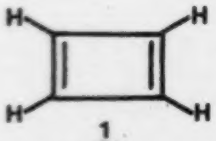
CYCLOBUTADIENE

CHAPTER 1

INTRODUCTION

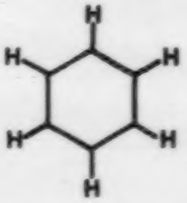
Early History

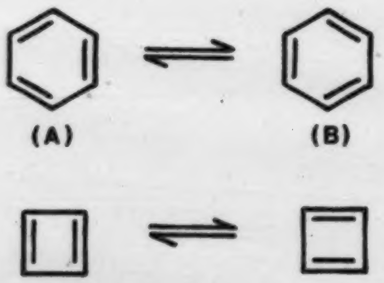
Cyclobutadiene 1 is the smallest member of the vinylogous series of hydrocarbons known as annulenes.[1] An [n]annulene is a monocyclic fully conjugated polyene of molecular formula $(CH)_n$ where n is even for the neutral species. Thus, cyclobutadiene, benzene, and cyclooctatetraene are [4]-, [6]-, and [8]annulene, respectively. Also many other higher vinylogues are known.[1b]



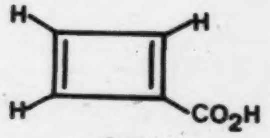
1

More than 100 years ago, Kekulé[2] proposed that the properties of the "aromatic compounds" could be explained by enclosing the six carbon atoms of the "benzene nucleus" in a totally symmetrical hexagon.





Later[3] he revised his formulation to the two alternating "Kekulé" structures (A) and (B), and expected cyclobutadiene to show similar behavior. It was in this connection that he attempted to prepare this molecule from crotonaldehyde. The experiment was unsuccessful. Similarly, in 1894, Perkin[4] failed in the preparation of cyclobutadienecarboxylic acid 2 and cyclobutadiene-1,2-dicarboxylic acid 3. Ten years later, Willstätter and Schmädel[5] again tried to synthesize the parent compound, but without success.



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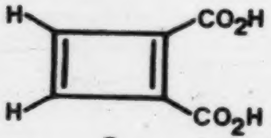


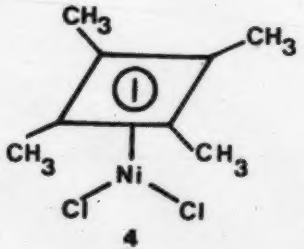
3

In spite of much effort, the period from 1915 to 1950 produced few positive results in the synthesis of cyclobutadiene and its derivatives, but a major theoretical step was taken.

In 1931, Hückel[6] applied the molecular orbital theory to the annulenes and arrived at his well-known rule for aromaticity. This rule predicted that a cyclic system containing $(4n+2)\pi$ electrons would exhibit aromatic properties and would be stabilized by electron delocalization, whereas a $(4n)\pi$ system would behave in the manner expected for polyenes. Therefore, it explained the chemical difference of cyclooctatetraene

([8]annulene), and benzene ([6]annulene), which had been found by Willstätter[7] in 1911. Since cyclobutadiene contains 4π electrons, the Hückel rule predicted that this molecule would not be stabilized by electron delocalization and accounted for the difficulties which had been encountered in its synthesis.

The molecular orbital theory advanced by Longuet-Higgins and Orgel[8] in 1956 predicted that cyclobutadiene should form stable complexes with transition metals, and the prediction renewed efforts to synthesize the molecule. Three years later, Criegee and Schröder[9] accomplished the first synthesis of a cyclobutadiene-nickel complex **4**. This was followed in 1965 by the preparation of a stable iron complex (**5**) of the parent.[10] Pettit and co-workers, who accomplished this synthesis,[10a] also reported[10b] that "free" cyclobutadiene could be generated from this complex by means of oxidizing agents. Thus, after almost one hundred years of effort the existence of cyclobutadiene as a definite chemical species appeared to be proven



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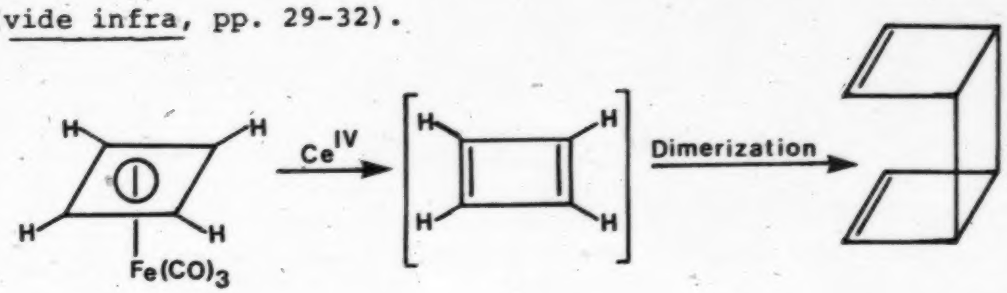
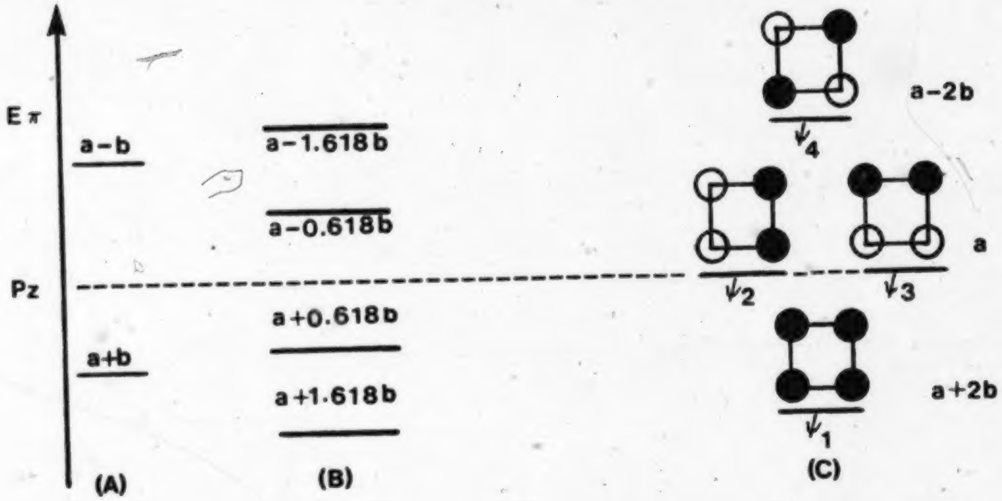
(*vide infra*, pp. 29-32).



5

1

In the meantime, the development of the theoretical treatment of conjugated molecules was continuing. In his application of the molecular orbital theory to cyclobutadiene, Hückel[6] assumed the molecule to have square geometry. This led to two of the four π electrons having to be accommodated in two degenerate, non-bonding molecular orbitals of energy a (Figure 1). In this case, there are four possible ways using the Pauli principle to assign the electrons to these orbitals, and all are degenerate in the Hückel approximation (Figure 2). However, non-linear molecules with orbitally degenerate electronic ground states in the Hückel scheme (*pseudo*-degeneracy), can be distorted in such a way that the degeneracy is removed. If this distortion results in stabilization, it is described as a Jahn-Teller effect.[11] Snyder,[12] in 1962 studied the result of distortions on hypothetical minimum-energy square cyclobutadiene. Using Hückel theory with the parameterization by Longuet-Higgins and Salem, he was able to show that a distor-


Eπ
a−b
a+b
a−1.618b
a−0.618b
a+0.618b
a+1.618b
Pz
a−2b
a
a+2b
ψ4
ψ2
ψ3
ψ1
(A)
(B)
(C)

a (Hii) = the Coulomb integral (the potential energy of an electron in the field of nucleus i).

b (H_{ij}) = the resonance or exchange integral (the energy of an electron in the field of two nuclei, i and j.

FIGURE 1. Hückel Energy-Level Diagram For π Energy For Ethylene (A), 1,3-Butadiene (B), and Square Cyclobutadiene (C).

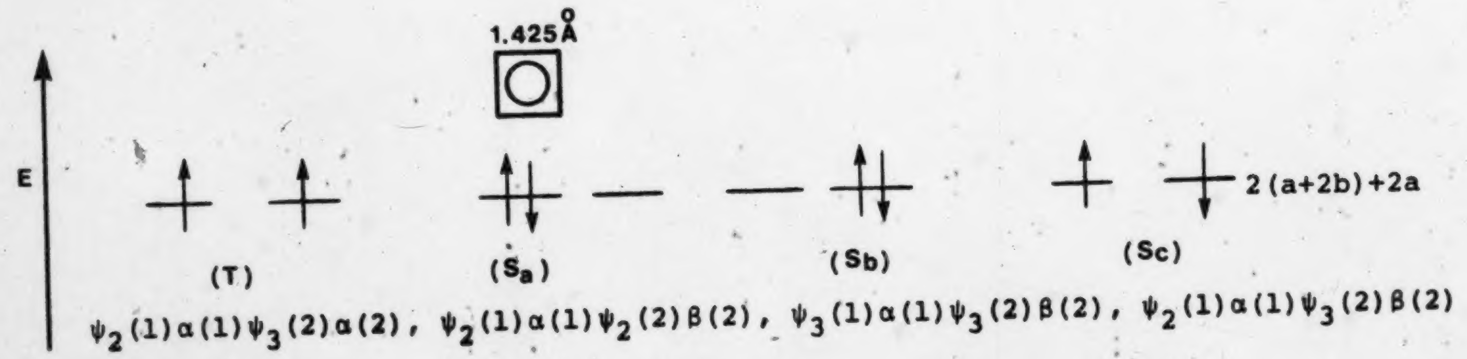

1.425 Å
E
2(a+2b)+2a
(T)
(Sa)
(Sb)
(Sc)
ψ2(1)α(1)ψ3(2)α(2), ψ2(1)α(1)ψ2(2)β(2), ψ3(1)α(1)ψ3(2)β(2), ψ2(1)α(1)ψ3(2)β(2)

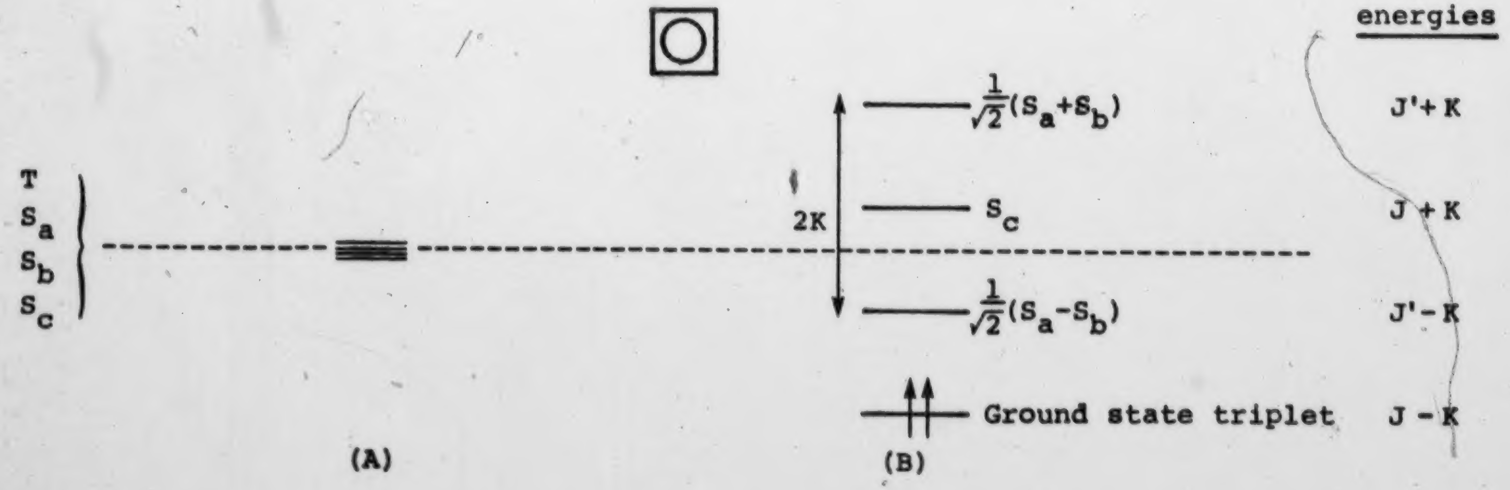
FIGURE 2. Schematic Representation of the Degenerate Electronic States of Square Cyclobutadiene in Simple Hückel Treatment (Only the Electrons in the Non-Bonding Molecular Orbitals ψ_2 and ψ_3 are Shown).

tion towards rectangular geometry resulted in stabilization of the molecule. The distortion energy was calculated to be -11.4 kcal/mol.

Snyder[12] further refined the calculation by introducing electron repulsion. When this effect was included the four degenerate electronic ground states of square cyclobutadiene were shown to split into different energy levels. If Hund's rule applies, the triplet state should be of lower energy (Figure 3). However, distortion of the appropriate symmetry towards a rectangle mixes the singlet states S_a and S_b to form another singlet ($c_1S_a - c_2S_b$) of energy lower than that of either S_a or S_b (Figure 4). For certain geometries, it was calculated that the energy of $c_1S_a - c_2S_b$ was lower than that of the lowest triplet (_pseudo_-Jahn-Teller effect,* Figure 5). According to this refined analysis, cyclobutadiene should exist in a rectangular structure with a closed

---

* If distortions, occurring in molecules without an orbitally degenerate ground state but having a low-lying electronic excited state, mix two states (generally, but not always, the ground and low-lying excited states) then the ground state energy may be lowered. Any resulting stabilization is called the _pseudo_ Jahn-Teller effect.[11,13]


T
S_a
S_b
S_c
2K
$\frac{1}{\sqrt{2}}(S_a+S_b)$
S_c
$\frac{1}{\sqrt{2}}(S_a-S_b)$
Ground state triplet
energies
J'+ K
J + K
J'- K
J - K
(A)
(B)

J = the Coulomb repulsion integral between electrons in different non-bonding orbitals.

J'(>J) = the Coulomb repulsion integral between electrons in the same non-bonding orbitals.

K = the exchange integral for two electrons with parallel spins in the two orbitals.

FIGURE 3. Lowest Triplet and Three Lowest Singlets of Symmetric Cyclobutadiene; (A) Simple Hückel Theory, (B) Electron Repulsion Included (Hund's Rule).[13]

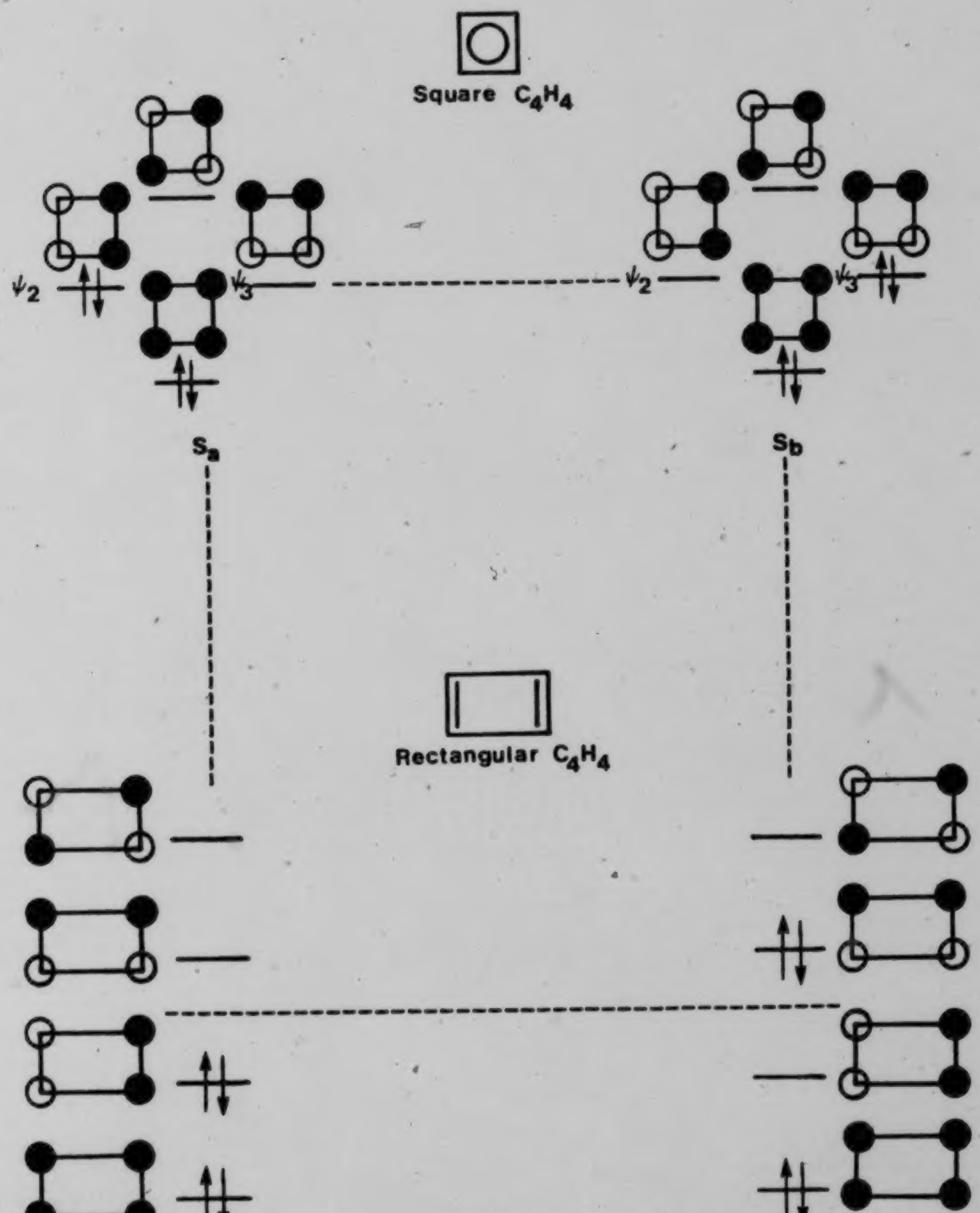

Square C4H4
ψ2
ψ3
ψ2
ψ3
Sa
Sb
Rectangular C4H4

FIGURE 4. Orbital-Energy Patterns for the Lowest and Highest Singlet of Planar Cyclobutadiene.

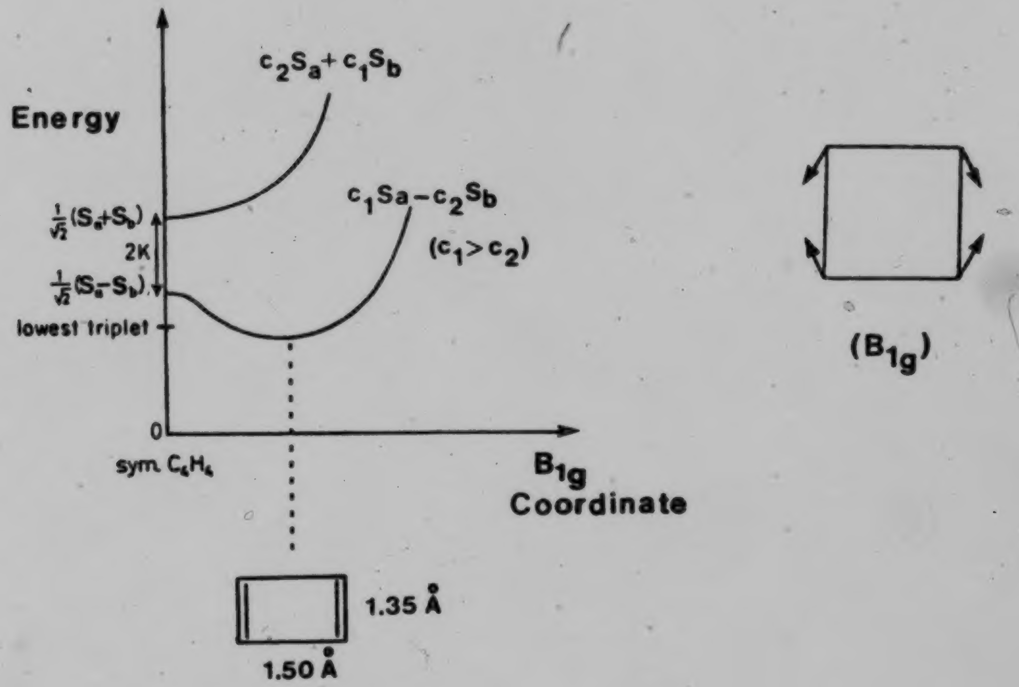

$c_2S_a + c_1S_b$
Energy
$\frac{1}{\sqrt{2}}(S_a+S_b)$
2K
$\frac{1}{\sqrt{2}}(S_a-S_b)$
lowest triplet
$c_1S_a - c_2S_b$
$(c_1 > c_2)$
0
sym. C_4H_4
B_{1g}
Coordinate
1.35 Å
1.50 Å
(B_{1g})

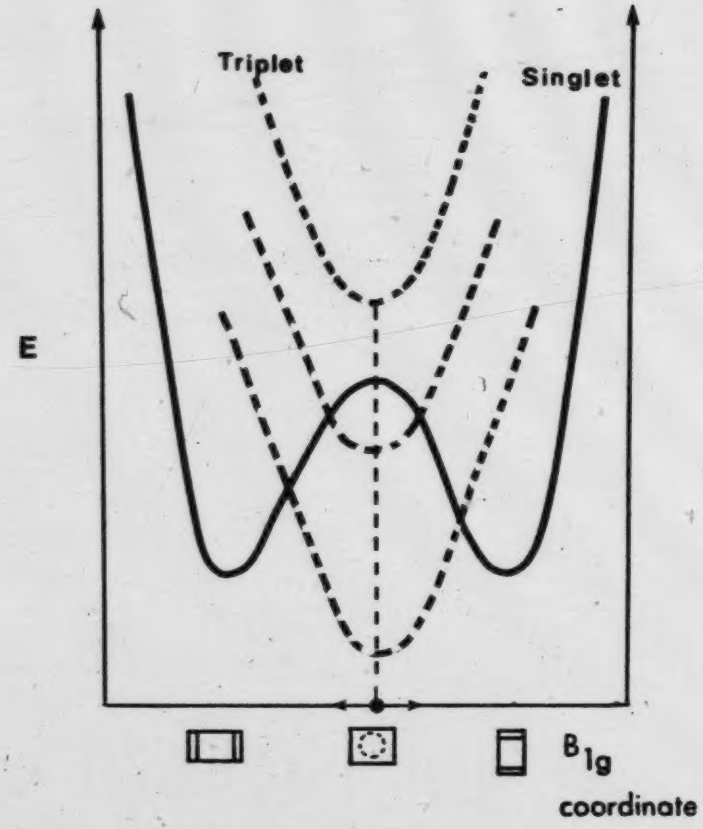
FIGURE 5. Pseudo-Jahn-Teller Stabilization of the Lowest Singlet State of Cyclobutadiene (The Splitting in the Symmetric Conformation is Due to Electronic Repulsion).[13]

shell singlet electronic ground state. The distortion energy was reduced from Snyder's earlier calculated value of -11.4 to only -1.3 kcal/mol. The molecule in the lowest triplet state was forecast to be most certainly square.

Snyder also showed that the bonds would be strongly interacting and predicted that, as a result of this interaction, the Raman spectrum of cyclobutadiene would show an unusually low antisymmetric stretching frequency relative to the symmetrical stretching frequency of the ring.[14] Similarly, in the infrared spectrum the two skeletal vibrations expected for a rectangular geometry would be widely separated. These predictions are significant in the light of later developments on cyclobutadiene chemistry.

Also during the 1960's the nature of the ground state of cyclobutadiene was investigated using a variety of different approximations.[15] All of them predicted a rectangular singlet molecule (RS) to be more stable than its square counterpart (SS) but were not consistent in predicting which of the two possibilities, square triplet (ST) or rectangular singlet (RS) would be the ground state (Figure 6).

The rather drastic approximations of these simpler methods are not made in ab initio calculations.[16] Although the massive computer programs required for this type of work have now evolved to the stage where, in principle, no molecule is beyond their capabilities, these calculations are still subject to some severe limitations.[17] The ab initio Hartree-Fock functions only approximately represent the reality of the molecular situation, since they do not take into account the instantaneous interactions of an electron with all others



1965	Dewar	1970	Figeys
1968	Allinger	1971	Dewar (MINDO-2)
1969	Dewar	1972	Hess
1970	Breslow	1973	Breslow

FIGURE 6. Energy Profiles of the Lowest Singlet and Triplet States of Cyclobutadiene by Various Approximate Methods.[15]

within the molecule.[*] Improvements in the calculation can be made by introducing "configuration interaction" (CI). In 1968, Buenker and Peyerimhoff[18] calculated the energy levels of cyclobutadiene for different geometries using ab initio SCF-MO calculations with extended CI. They found that the singlet lay below the triplet at all geometries studied. The energy profile for the singlet showed minima at two possible rectangular conformations and a maximum at the square conformation, while that for the triplet was a minimum for square geometry (Figure 7).

Allinger[15b] in the same year, using Pariser-Parr functions with doubly excited CI reached a conclusion similar to that of Buenker and Peyerimhoff (Figure 7). In contrast, more recently, Newton,[19] using the ab initio SCF method with 4-31G functions found that the triplet potential energy surface crossed that of the singlet and, for a square geometry, the triplet was of lower energy than the singlet (Figure 7). However, Newton had not included CI in his calculations and it is now accepted that this refinement lowers the energy of the singlet more than that of the triplet. This

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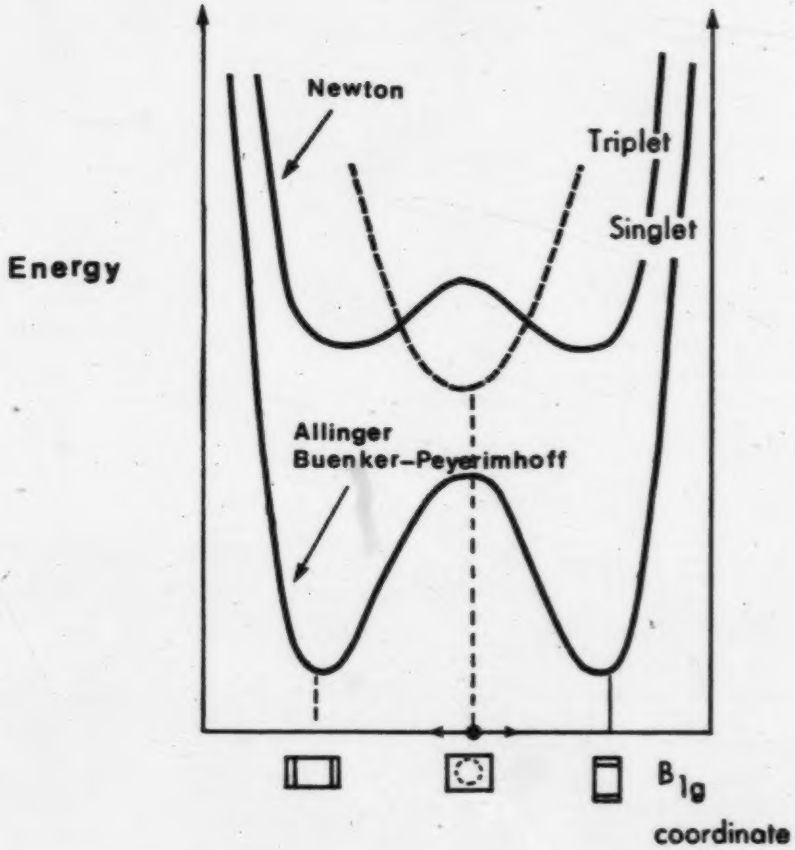
[*] In reality, an electron in an atom will have instantaneous interactions with all the other electrons. These will not be the same as the average interaction included in the SCF procedure.



1968 Allinger[15b]

1968 Buenker-Peyerimhoff[18]

1973 Newton[19]

FIGURE 7. Ab initio SCF Energy Profiles of the Lowest Singlet and Triplet States of Cyclobutadiene.

particular aspect will be discussed in more detail subsequently.

The foregoing discussion describes the history of the chemistry of cyclobutadiene from its inception to the early 1970's when investigation on this topic began in this laboratory. Since more recent developments have had an important bearing on the present study, they will be elaborated in more detail in the following chapter.

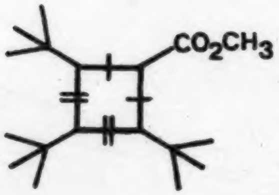
CHAPTER II

RECENT DEVELOPMENTS

The generation of short-lived "free" cyclobutadiene from a stable iron complex by Pettit and coworkers[10] marked a turning point in the history of that molecule. This experiment almost assured that cyclobutadiene was extremely reactive, especially towards dimerization. Thus, its reactivity precluded the isolation and purification of the molecule under normal laboratory conditions, and use of an X-ray analysis for the determination of the structure of cyclobutadiene was definitely not feasible. However, two approaches appeared possible in order to suppress the dimerization and allow chemical investigation of the molecule.[20] One was the isolation of the monomeric compound within a rigid matrix at cryogenic temperatures which would permit a spectroscopic analysis. The second involved the preparation of derivatives carrying bulky substituents which would sterically hinder dimerization of monomers. These derivatives should be isolable in crystalline form and so be amenable to X-ray analysis. These two approaches have been adopted and have provided interesting results. For the sake of clarity, the information obtained from cyclobutadiene derivatives will be outlined first, and then the chemistry of the parent compound along with the theoretical interpretation of the results will be summarized.

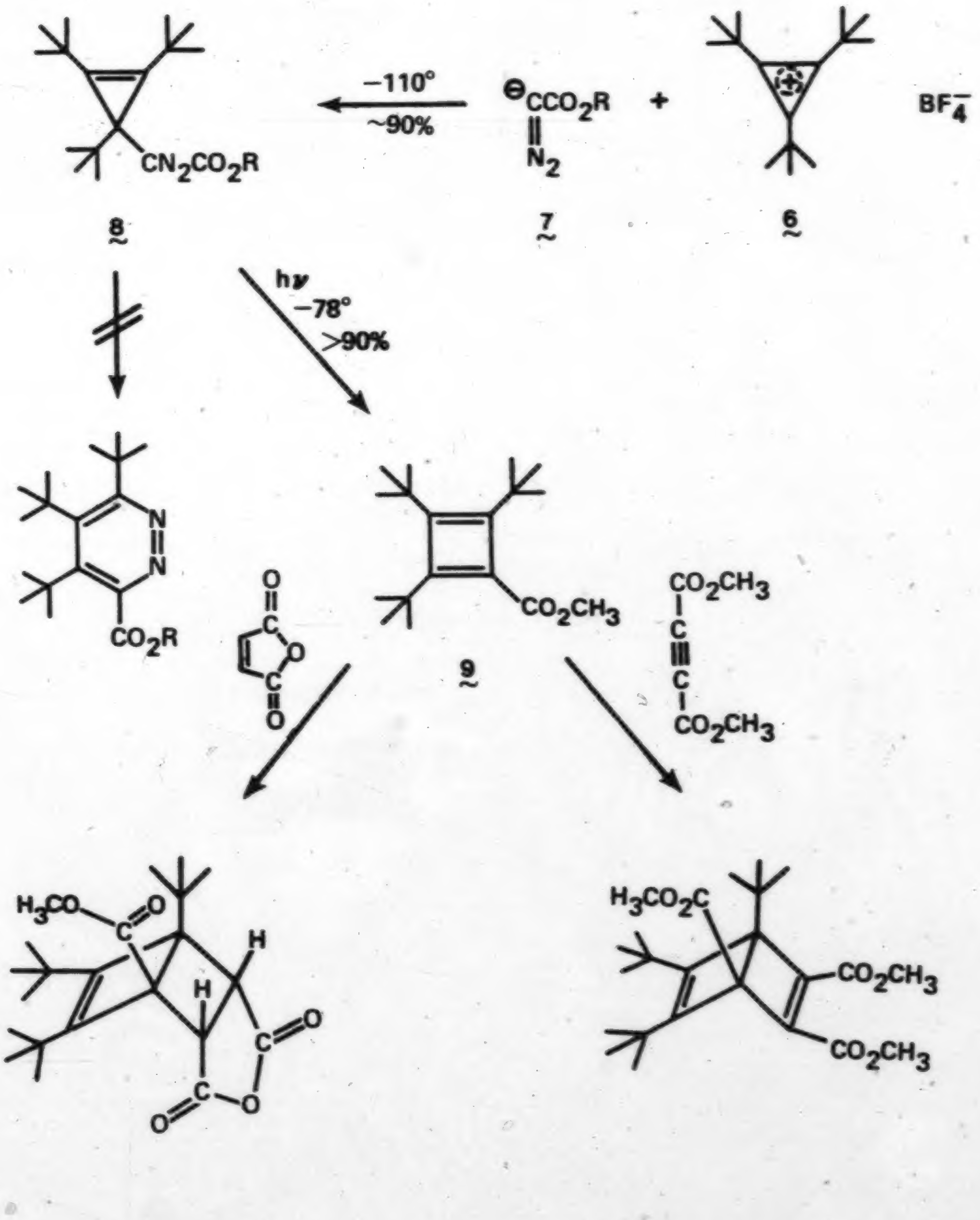
2.1 Cyclobutadiene Derivatives

The synthesis of isolable, crystalline derivatives of cyclobutadiene has been carried out in this laboratory. In selecting appropriate derivatives, two basic conditions were considered.[20] Firstly, the substituents had to be sufficiently bulky to suppress dimerization, and secondly, the substitution pattern had to be chosen in such a way as to preserve as far as possible the symmetry and ground state properties of the parent. Data accumulated in the laboratory suggested that methyl tri-tert-butylcyclobutadienecarboxylate (9) fulfilled

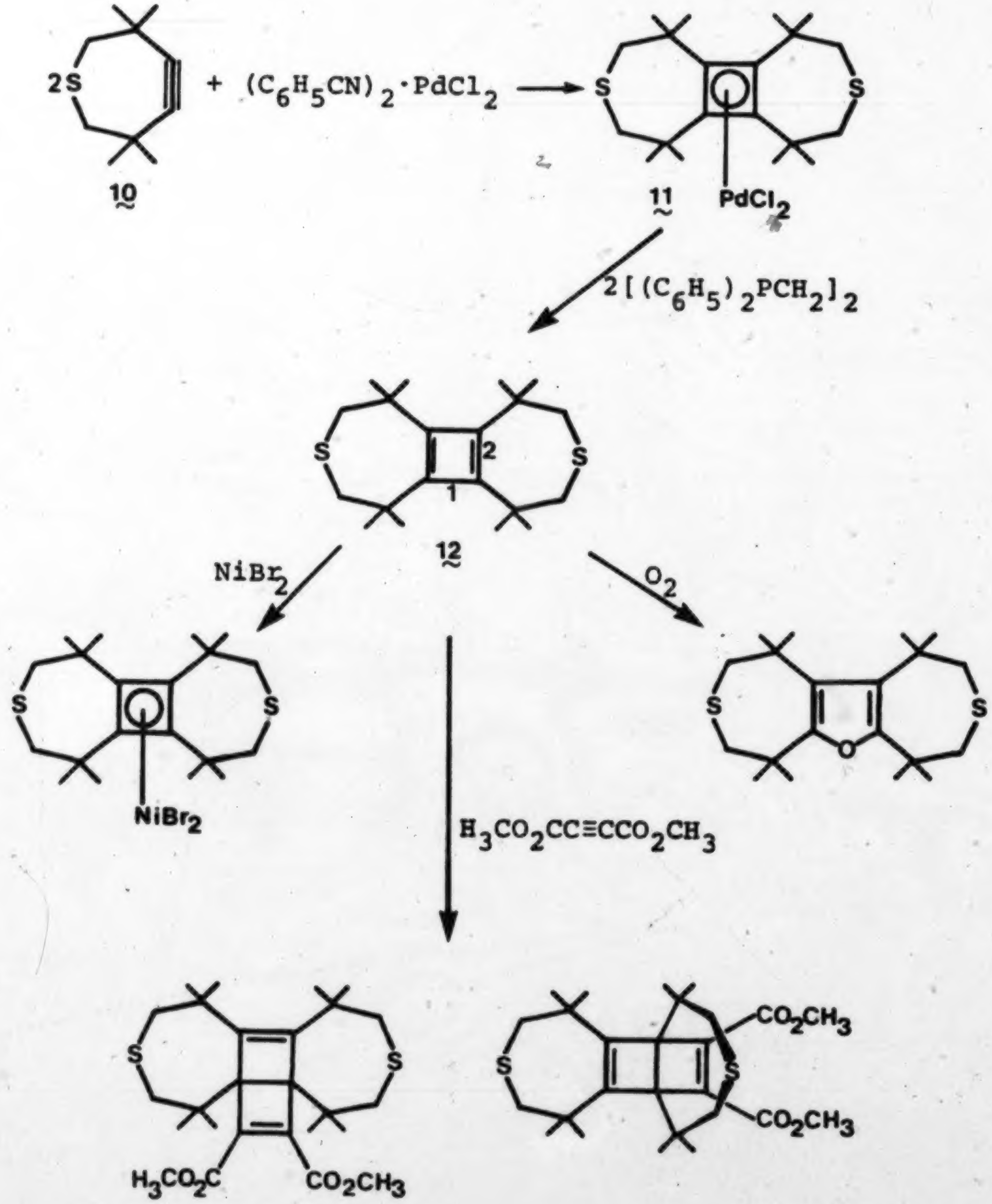


9

these conditions. A number of routes leading to its synthesis were examined, and it was found that the well-known ring expansion method utilizing cyclopropenylmethylene proceeded well with highly substituted precursors. Reaction of tri-tert-butylcyclopropenium fluoroborate (6) with the anion of methyl diazoacetate (7) gave 8 as a stable compound. Photolysis of 8 proceeded smoothly at -78°C to afford 9, a stable, crystalline compound.[21]

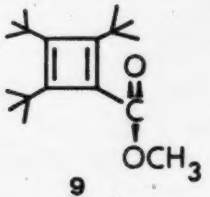

−110°
~90%
⊖CCO2R
N2
+
BF4−
CN2CO2R
8
7
6
hν
−78°
>90%
CO2R
CO2CH3
9
CO2CH3
CO2CH3
H3CO
H
H
H3CO2C
CO2CH3
CO2CH3

Concurrently, Kimling and Krebs[22] were studying octamethyldithiepinocyclobutadiene (12). They synthesized compound 12 from 3,3,6,6-tetramethyl-1-thiacyclo-

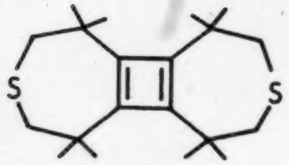

2S
+ $(C_6H_5CN)_2 \cdot PdCl_2$
S
S
10
11
$PdCl_2$
$2[(C_6H_5)_2PCH_2]_2$
S
2
1
S
12
$NiBr_2$
O_2
S
S
$NiBr_2$
S
O
S
$H_3CO_2CC{\equiv}CCO_2CH_3$
S
S
H_3CO_2C
CO_2CH_3
S
S
CO_2CH_3
CO_2CH_3

heptyne 10 and $(C_6H_5CN)_2PdCl_2$ to give the cyclobutadiene complex 11 which was subsequently decomposed with ethylenebis-(diphenylphosphane). Although this derivative was also crystalline, it had a drawback in that the substitution pattern was such that the two bonds sharing one carbon atom of cyclobutadiene (1 and 2) were not equivalent as far as the π-electron system was concerned. Table 1 summarizes the physical data of both compounds, 9 and 12. The ground-state geometry of compounds 9 and 12 was determined directly by X-ray crystallographic analysis (Figure 8). The π system of the methoxycarbonyl group of 9 was shown to be orthogonal to that of the ring system. Thus, there should be very little interaction between the ring π electrons and those of the carbonyl group. Also, steric interactions between the tert-butyl groups appear to cause only slight distortion of the ring geometry. In fact the ring was shown to be a slightly distorted rectangle having bond angles close to 90° and sides of length 1.406 and 1.376, and 1.547 and 1.506 Å.[23]

The X-ray analysis of 12 was performed by Irngartinger and Rodewald.[24] Again, the ring was found to have rectangular geometry. For both derivatives, 9 and 12, no esr signals are observed and the lines of the nmr spectra are sharp. Furthermore, there is no strong absorption in the uv above 300 nm. Allinger's calculation[15b] concludes that if cyclobutadiene had a triplet ground state, it



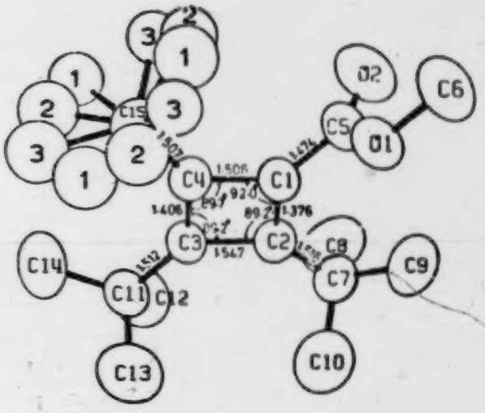
9



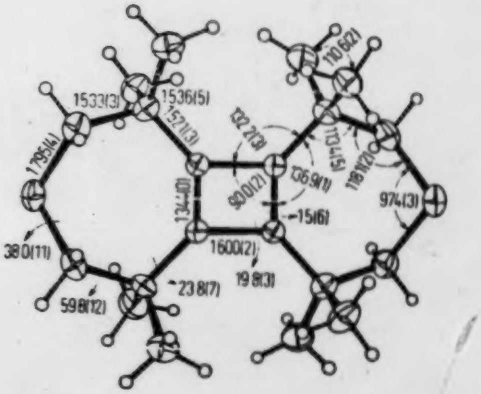
12

mp: 70.0°	240°
uv: 425 nm (ε = 47)	227 nm
^{1}H nmr, 60 MHz (methylcyclohexane-$\underline{d}_{14}$) δ: 3.45 (s, 3), 1.19 (s, 9), 1.13 (s, 18)	(CDCl$_3$) δ: 2.50 (s, 8), 1.26 (s, 24)
(methylcyclohexane-$\underline{d}_{14}$) δ: 29.73 ($\underline{CH}_3$-C), 31.6, 31.8 (Cquat of $\underline{t}$-Bu), 50.4 (O-CH$_3$), 147.0 (C-3), 154.5 (C-1 overlaps with C-2 and C-4), 165.7 (C=O)	^{13}C nmr, 22.63 MHz (CDCl$_3$) δ: 27.0 (CH$_3$), 41.6 (Cquat), 52.1 (CH$_2$), 146.5 (Colef)
ir (pentane): 1716 cm^{-1} (s)	Raman (cryst): ν C=C 1590 cm^{-1}
Sublimes at 50° (10 mTorr)	mass spectrum (m/e): 336 (M+), 321 (M-CH$_3$), 280 (M-C$_4$H$_8$), 265 (M-CH$_3$, -C$_4$H$_8$), 209 (M-CH$_3$, - 2C$_4$H$_8$),
Oxygen sensitive	Very sensitive towards oxygen.

TABLE 1. Physical Data and Reactivity for 9[21] and 12[22].


2
3
1
1
2
C15
3
3
2
1
O2
C6
C5
O1
1.502
1.506
1.474
C4
92.0
C1
1.406
89.7
89.2
1.376
89.2
C3
1.547
C2
1.515
C8
C14
1.512
C7
C9
C11
C12
C13
C10

9

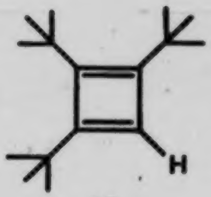

1533(3)
1536(5)
1521(3)
132.2(3)
110.6(2)
113.4(5)
118.1(2)
1795(4)
136.9(1)
90.0(2)
134.4(1)
97.4(3)
-15(6)
380(11)
1600(2)
19.8(3)
-23.8(7)
59.8(12)

12

FIGURE 8. Selected Bond Distances and Angles (Averaged) of Methyl Tri-tert-butylcyclobutadienecarboxylate (9) and Octamethyldithiepinocyclobutadiene (12).

would show a strong absorption at 380 nm. Therefore, all the evidence consistently shows that the ground state of these derivatives of cyclobutadiene is a rectangular singlet.

The chemical shift of a proton directly attached to



15

a cyclic π-electron system provides important information about the nature of the induced ring current,[25] a criterion that has often been used to evaluate the aromaticity (or anti-aromaticity) of the system.[*] For this purpose, tri-*tert*-butylcyclobutadiene (15) was chosen and synthesized as outlined below. The tetrafluoroborate 6 was converted into the corresponding cyano derivative which in turn was reduced with lithium aluminum hydride to provide amine 13. The diazo compound 14 was prepared from this amine and the photocleavage of 14 either in methylcyclohexane or tetrahydrofuran at -70°C provided the desired tri-*tert*-butylcyclobutadiene (15).[21] In contrast to the methoxy-

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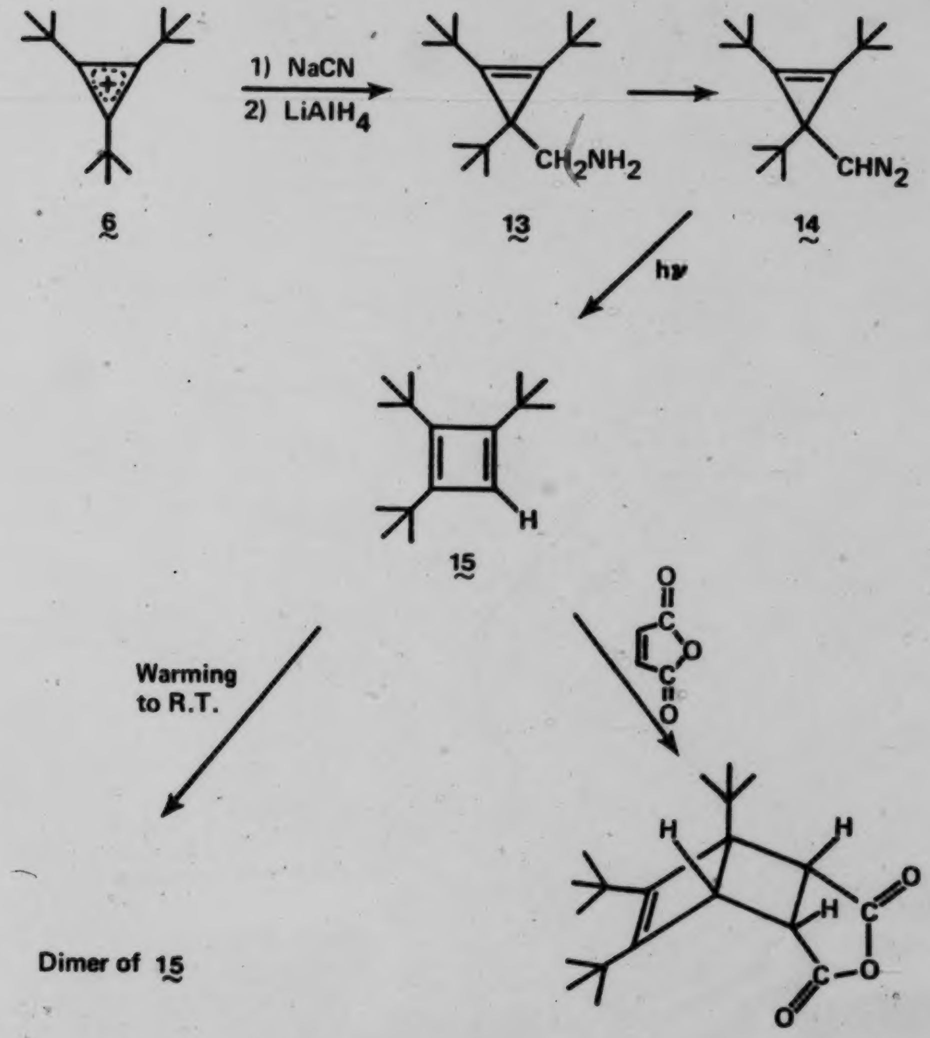
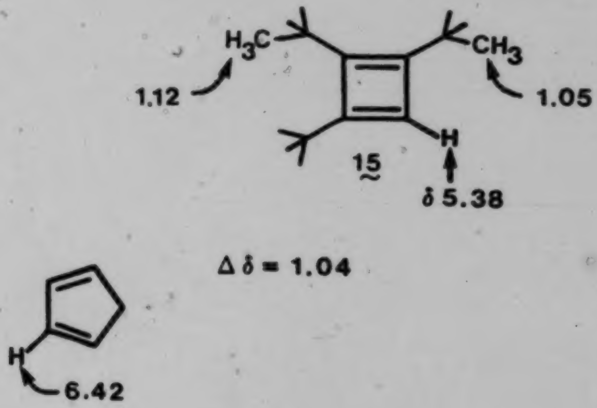
[*] ^{13}C nmr absorptions are relatively insensitive to ring current effects[26] and the spectral data of the fully substituted derivatives, 9 and 12, are not informative in this respect.


1) NaCN
2) LiAlH$_4$
CH$_2$NH$_2$
CHN$_2$
6
13
14
hν
H
15
Warming to R.T.
Dimer of 15
O
C
O
C
O
H
H
H
O
C
O
C
O

carbonyl derivative (9), compound 15 dimerized on warming to room temperature and this precluded further purification. When the progress of the photolysis of the diazo compound 14 at -70°C was monitored by ^1H nmr spectroscopy at low temperature, the tri-tert-butyl derivative 15 showed absorptions as indicated below. The proton at carbon 2 of cyclopentadiene (δ 6.42) was



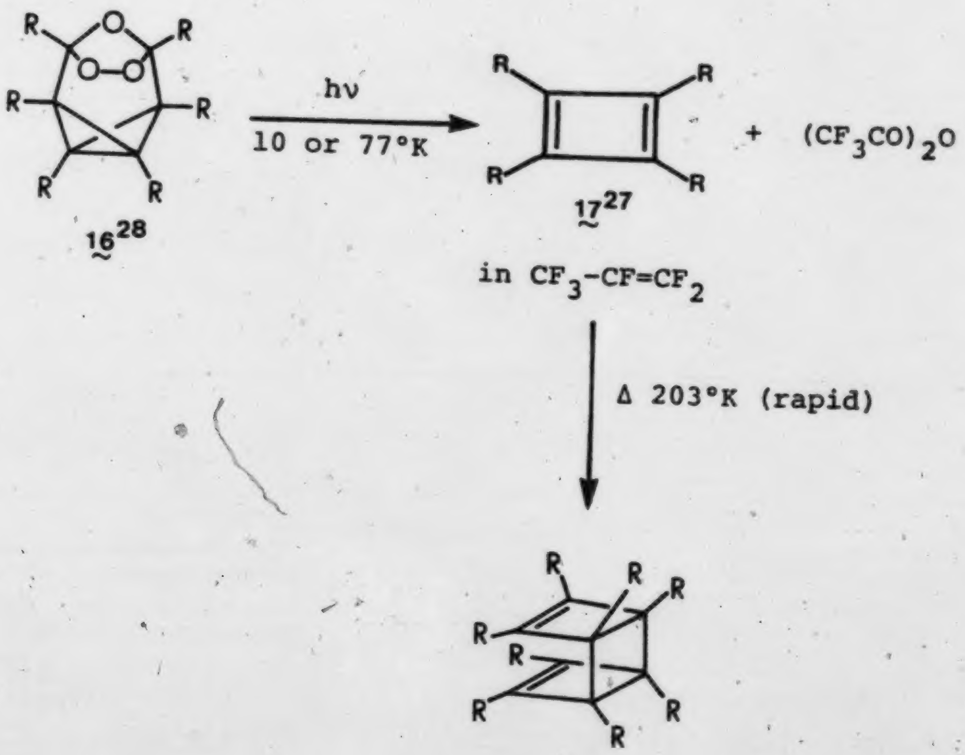
Pople-Untch equation:

$$l = -(\pi^2 e^2 \beta_o / h^2 c) S (32 \lambda^{\frac{1}{2}} M^2) \times \sum_{j}^{occ} [1 + 2\lambda \cos(4\pi j/M) + \lambda^2]^{-3} [\lambda + (1 + \lambda^2) \times \cos(4\pi j/M) + \lambda \cos^2(4\pi j/M)]$$

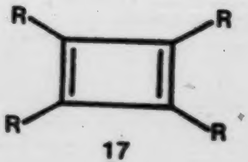
used as reference. Then, the difference, Δδ = 1.04 (6.42-5.38), was taken as the paramagnetic contribution of the induced ring current. Using several assumptions, including, the rectangular geometry for the parent calculated by Dewar (MINDO-2),[15k] the Pople-Untch equation[25] gave a paramagnetic contribution of 1.18 ppm for the system. The agreement between the experimental and calculated values is excellent, although it is subject to the arbitrary choice of the reference compound.

In addition to the nmr spectrum, the infrared spectrum of compound 15 isolated in an argon matrix at 4.2°K was measured.[20] No absorption between 1700 and 1490 cm^{-1} could be observed, indicating that under these conditions the system does not exhibit a noticeable normal C=C stretching vibration.

The full spectral characterization of a symmetrically substituted derivative, tetrakis-(trifluoromethyl)-cyclobutadiene (17),[27] has also been accomplished. Irradiation of ozonide 16[28] in a hexafluoropropene matrix at 77°K led to the almost exclusive formation of 17 and trifluoroacetic anhydride. After thawing the matrix, 17 had a half-life of approximately 6 h at 130°K and dimerized rapidly at 203°K (Figure 9). The trifluoromethyl group is very likely to be the smallest substituent which suppresses the dimerization sufficiently to permit spectral measurements of a monomeric cyclobutadiene derivative in solution. The uv spectrum of the photolysate of 16 recorded at 130°K shows only a very weak, forbidden absorption at about 375 nm ($\varepsilon = 20$), which again strongly suggests a singlet ground state for the molecule if Allinger's prediction is accepted (vide supra). The infrared spectra of 17 showed the presence of a strong band at 1700 cm^{-1}. If the assignment of this band to a C=C stretching vibration proves to be correct, then the geometry of 17 is not square, but very likely rectangular.


R
O
O–O
hν
10 or 77°K
+ $(CF_3CO)_2O$
in CF_3-CF=CF_2
Δ 203°K (rapid)

$\mathbf{16}^{28}$ $\mathbf{17}^{27}$



$\mathbf{17}$

R = CF_3

^{19}F nmr (hexafluoropropene) δ: 69.0

^{13}C nmr (hexafluoropropene) δ: 135.7

uv (hexafluoropropene): 375 nm (ε = 20)

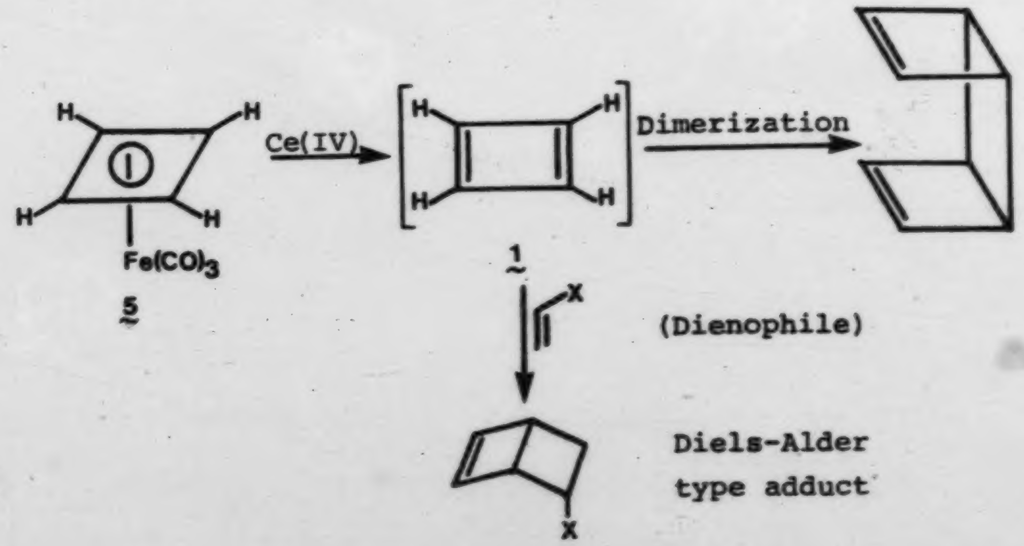
ir (3-methylpentane matrix) cm^{-1}: 1700

FIGURE 9

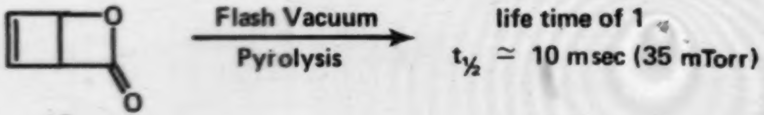
2.2 Parent Species

The preceding section describes that the ground states of the monomeric cyclobutadiene derivatives 9 and 12 are singlet and that their geometry is not square but rectangular. The extrapolation of these results to the parent compound (1), however, should be made only with reservation. As suggested by the inconsistency of several recent theoretical calculations,[15] the ground state appears to represent a "shallow well" of the energy surface of the cyclobutadiene system, and further, even the simple substituents in 9 and 12 could possibly perturb the system in a significant manner. Therefore, the elucidation of the spin multiplicity and exact geometry of ground state cyclobutadiene must rely upon direct studies on the properties of the parent molecule.

Since Pettit[10b] first reported the oxidative genera-



tion of cyclobutadiene in 1965, there have been performed numerous experiments to define the properties of this species. Flash photolysis of cyclobutadieneiron tricarbonyl (5) in the gas phase was carried out in this Department in 1967.[29] The cyclobutadiene so generated was detected by kinetic mass spectrometry. This allowed the measurement of the lifetime of the molecule ($t_{1/2}$ = 2 msec at 100 mTorr). In the following year, Hedaya and co-workers[30] performed flash-vacuum pyrolysis on photo-α-pyrone (18)* and concluded that the half-life was approximately 10 msec at 35 mTorr, in accord with the previous finding. Hence, cyclobutadiene (1), although very reactive, clearly possessed a definite lifetime as a chemical species. In 1973 Schmidt[32a] and independently Grubbs and Grey,[32b] substantiated Pettit's[10b] original claim of the transient generation of "free" cyclobutadiene. It was shown that when an optically active



18

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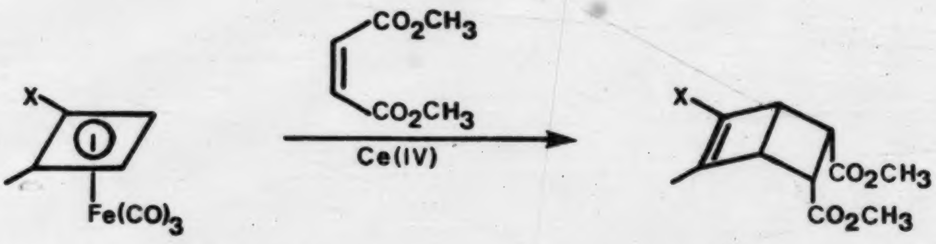
[*] Photo-α-pyrone was first synthesized and characterized by Corey[31] in 1964 who remarked at the time that it should be an ideal precursor for the generation of cyclobutadiene.

cyclobutadiene complex (19a or 19b) was oxidatively

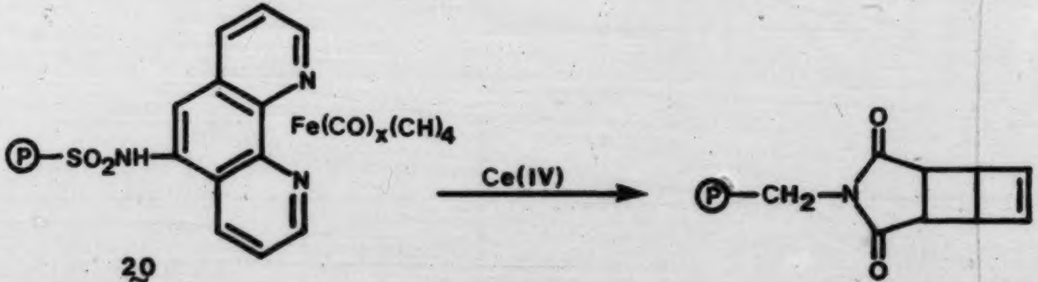

X
Fe(CO)$_3$
CO$_2$CH$_3$
CO$_2$CH$_3$
Ce(IV)
X
CO$_2$CH$_3$
CO$_2$CH$_3$

19a, X = CH_2CH_3 Schmidt

19b, X = CH_2OCH_3 Grubbs-Grey

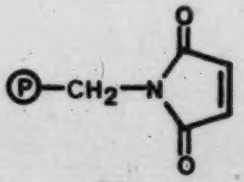
Racemate

decomposed in the presence of a symmetrical dienophile the adducts were racemic. Consequently, the cyclobutadiene ligand reacted after it had gained a plane of symmetry. This indicates that the metal is not close enough to the ligand to maintain the original chiral surrounding of the complex. Rebek[32c] treated cyclobutadieneiron carbonyl held on a polymer support (20) with Ce(IV) in the presence of maleimide which was also attached to a support (21). The iron complex was


P
SO$_2$NH
N
N
Fe(CO)$_x$(CH)$_4$
Ce(IV)
P
CH$_2$
N
O
O

20

22

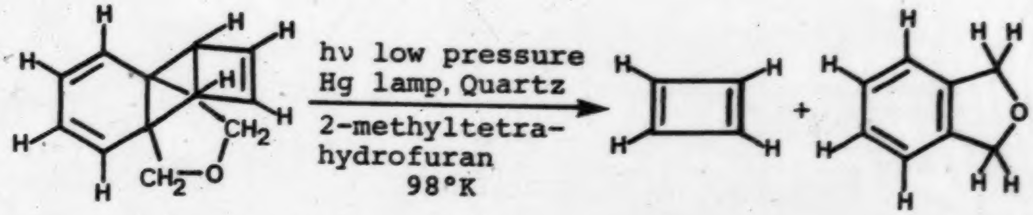


21

oxidized and **22** resulted. Therefore, free cyclobutadiene was transferred from the polymer containing the complex (**20**) to the polymer containing the trapping agent (**21**), a proof of a finite lifetime for cyclobutadiene (**1**).

Further characterization of the species required suppression of the strong tendency of the molecule to dimerize. Generation of monomeric cyclobutadiene in a rigid matrix at cryogenic temperatures was a method by which this could be accomplished. This matrix-isolation technique was developed in the 1950's by Pimentel[33] at Berkeley for the study of unstable and reactive chemical species. It involves the immobilization at a very low temperature of the species of interest within a rigid cage of a chemically inert substance (the matrix). In this way monomeric cyclobutadiene has been generated photochemically from matrix-isolated precursors. The rigidity of the cage prevents diffusion of the molecule, suppressing dimerization. The cold temperature, besides contributing to the rigidity of the cage, also serves to reduce the rate of possible rearrangements that require activation energy. Under such conditions, cyclobutadiene can be preserved indefinitely and intensively studied. However, X-ray crystallographic methods cannot be applied to matrix-isolated compounds which are, by the very nature of the technique, in a noncrystalline form. Consequently, we must have recourse to other methods in order to characterize the species as completely as possible.

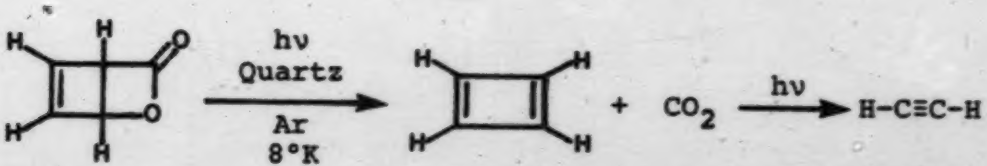
Some spectral data of cyclobutadiene (1) isolated in a matrix have been obtained. In 1972 in this laboratory,[34] 1 was generated in a 2-methyltetrahydrofuran matrix at 98°K by photocleavage of the tetracyclic


hν low pressure
Hg lamp, Quartz
2-methyltetrahydrofuran
98°K

23a 1 24a

uv: 300-305 nm (ε = 100)

ether 23a. Its ultraviolet spectrum was recorded. The spectrum showed only a forbidden transition at 300-305 nm (ε = 100), in agreement with Allinger's prediction for a singlet ground state (vide supra). Concurrently, Lin and Krantz[35] measured the infrared spectrum of the photolysate arising from matrix-isolated photo-α-pyrone (18). Bands in the spectrum at 1236, 653 and 573 cm^{-1}

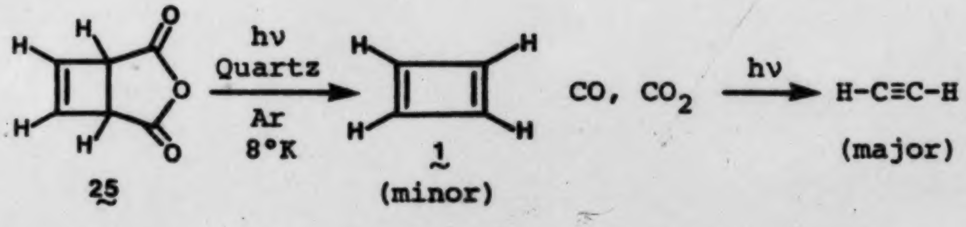

hν
Quartz
Ar
8°K
+ CO_2
hν
H-C≡C-H

18 1 (minor) (major)

were attributed to cyclobutadiene. Also present in the spectrum were bands at 2340 and 660 cm^{-1} assigned to CO_2. The following year, using the same precursor, Chapman, McIntosh and Pacansky[36] independently observed a very similar spectrum (Table 2). As will be further explained later (Chapter III), it can be predicted from group theory that if cyclobutadiene is square, four modes of vibration are infrared active, while if it is rectangular, seven modes are infrared active. The simplicity of the observed infrared spectrum led Chapman to the tentative conclusion that cyclobutadiene had square geometry. Subsequently, Krantz, Lin and Newton[19] also concluded that the spectrum was "most compatible" with a square structure based on the appearance of only three bands below 2000 cm^{-1}. They further maintained that the location of these bands was consistent with a square geometry. In particular, the band at 1236 cm^{-1} "lying in between the limits of the usual C=C (1650 cm^{-1}) and C-C (1000 cm^{-1}) vibrations", was assigned to predominantly the in-plane ring deformation mode (ν_2). Support for the spectral assignments was provided by normal coordinate calculations on cyclobutadiene ($\underset{\sim}{1}$) and on its monodeuterio derivative. In addition, theoretical considerations by Newton (_vide infra_) led these authors to favor a triplet state for the observed species.

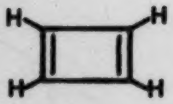
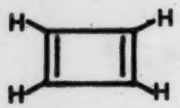
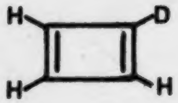
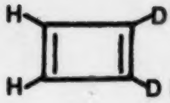
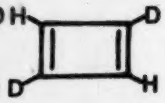
In 1973, Chapman and co-workers[37] published infrared spectra attributed to monodeuterio-, 1,2-dideuterio-, and 1,3-dideuteriocyclobutadienes. These compounds were generated by photofragmentation of the appropriate photo-α-pyrones, and the spectra were considered by Chapman to fit his earlier tentative conclusion that cyclobutadiene had square geometry (Table 2).

Three years later, Maier, Hartan and Sayrac[38] used a different precursor to yield cyclobutadiene. They irradiated cyclobutenedicarboxylic anhydride (25) isolated in an argon matrix and were able to record an infrared spectrum of the photolysate which was essentially the same as that which had been observed from the fragmentation products of photo-α-pyrone (18).[35,36] However, when the tetracyclic ether 23a was photolyzed,



Infrared (cm^{-1}): 1237-1241, 653 and 573.

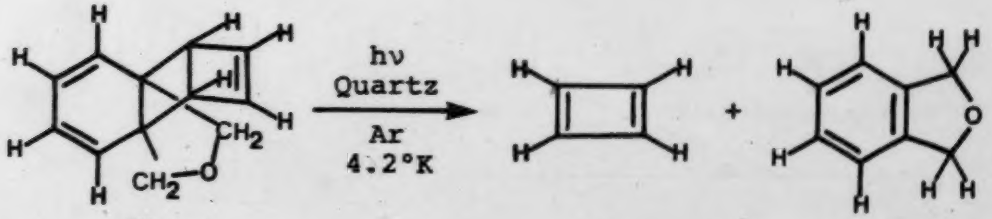
a process known to yield cyclobutadiene,[34] the infrared spectrum lacked the band at 650 cm^{-1} attributed to cyclobutadiene. In this case, only two intense, single absorptions at 1240 and 570 cm^{-1} were observed both

Lin-Krantz		Chapman et al.	Krantz-Lin[19]	Chapman[37]	Chapman[37]	
Experimental[35]	Calculated[19]	Experimental[36]	Experimental		Experimental	
-	3000	3040	-	-	-	-
1236	1236	1240	-	-	-	-
-	-	-	1224	1223	1212	1216
-	-	-	-	-	1188	1182
-	-	-	(780)	780	770	781
653	661	650	653	654	654	654
-	-	-	-	-	-	633
573	576	570	594	583-576	583-576	583-576
-	-	-	540	535	-	535
-	-	-	460	-	-	-

TABLE 2. Infrared Absorptions of Cyclobutadiene and Its Mono- and Dideuterio Derivatives (cm^{-1}).

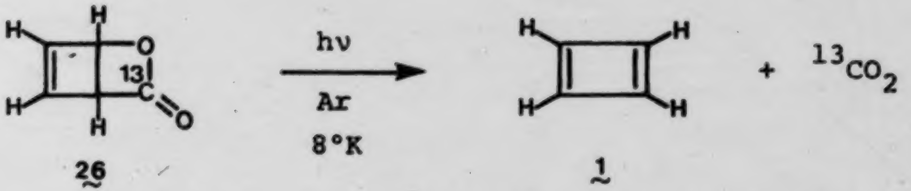
by Masamune and co-workers[39] and by Maier and co-workers.[38] An explanation for the presence of a band at 650 cm^{-1} comes from evidence accumulated by Maier[40] that cyclobutadiene tends to form complexes with species such as CO_2 that possess electron acceptor properties. Therefore, the CO_2 generated from 18 or 25 and located in the neighborhood of 1 may interact with 1 causing a splitting (650 and 660 cm^{-1}) of the band at 663 associated with the bending vibration of CO_2. Irradiation of the ether 23a gives as a by-product phthalan (24a), which does not



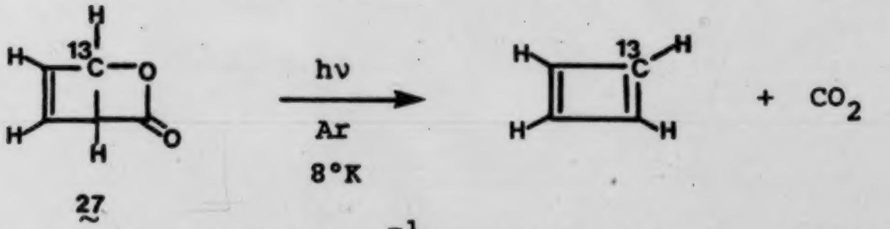
23a 1 24a

Infrared (cm^{-1}): 1240, 570

act as an electron acceptor. Hence, the band at 650 cm^{-1} appears only when CO_2 is generated as a by-product of the photolysis and so it is not attributable to a vibration of cyclobutadiene (1). This conclusion was corroborated later by Pong, Huan, Laureni, and Krantz[41] by an analysis of the infrared spectra of the photolysates of [2-^{13}C]- and [6-^{13}C]-photo-α-pyrones (26 and 27). In this paper on ^{13}C-labelled photo-α-pyrones, Krantz emphasized that the most notable feature in the

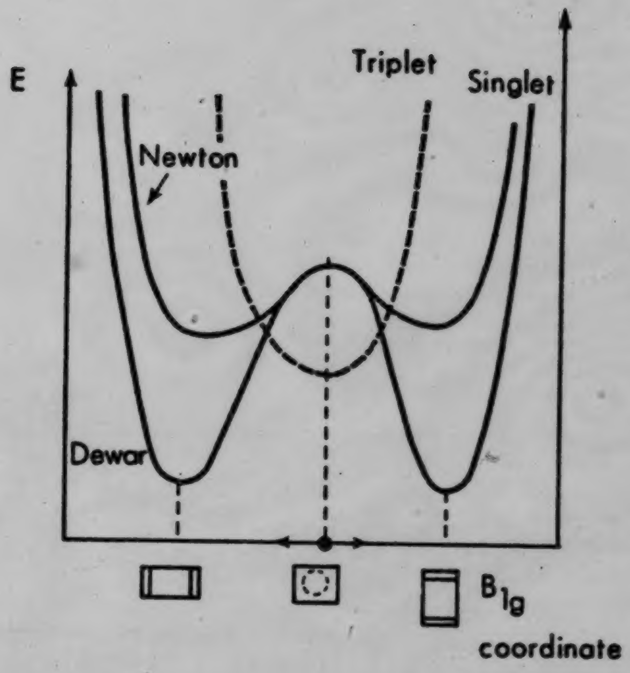


Infrared (cm^{-1}): 1241, 575 644, 636



Infrared (cm^{-1}): 1237, 575 622, 655

spectrum of the photolysate from 27 was "the slight shift of the 1241 cm^{-1} band of 1 to 1237 cm^{-1} ..., in accordance with the original assignment of this band to a predominantly framework distortion of 1." (*vide supra*). Thus, he continued to maintain that the position of the bands in the infrared spectrum of cyclobutadiene was consistent with square geometry. If the molecule is square, it follows from Newton's[19] *ab initio* SCF calculations that it should be a triplet. Newton stressed that "calculations using the general valence bond method (GVB) indicate that the singlet lies 7.7 kcal/mol above the triplet at the triplet equilibrium geometry and is unstable to a rectangular distortion." Therefore, it is concluded that for square geometry the triplet would be of lower energy than the singlet. However, repeated attempts to observe esr signals which may be ascribed to triplet cyclobutadiene have consistently failed; the uv spectra have shown only forbidden transitions at around 300 nm (vide supra), and the derivatives examined have been found to be rectangular and most probably to have a singlet ground state. Later, Dewar[42] suggested that esr signals might be difficult to detect in the case of cyclobutadiene and also showed, on the basis of his MINDO-3 calculations, that the energy level of the square singlet structure would lie well above that of the square triplet (by 13.1 kcal/mol). In addition he calculated that the intersection of the singlet and triplet energy surfaces would lie above the triplet minimum and thus, conversion of the square triplet to singlet would require an activation energy of 2.3 to 3.5 kcal/mol (Figure 10). The interconversion would be completely suppressed by an energy barrier of this height at the temperatures used in the matrix-isolation experiments (4.2 to 10°K). In order to explain the infrared spectra of Lin and Krantz[35] and of Chapman and co-workers,[36] Dewar proposed that the species observed at those temperatures could have been the square triplet, an excited state and not the ground state. It was found in this laboratory, however, that the infrared spectrum of cyclobutadiene measured at 110°K in dichloromethane matrices did not differ significantly from that measured at 4.2°K


E
Triplet
Singlet
Newton
Dewar
B_{1g}
coordinate

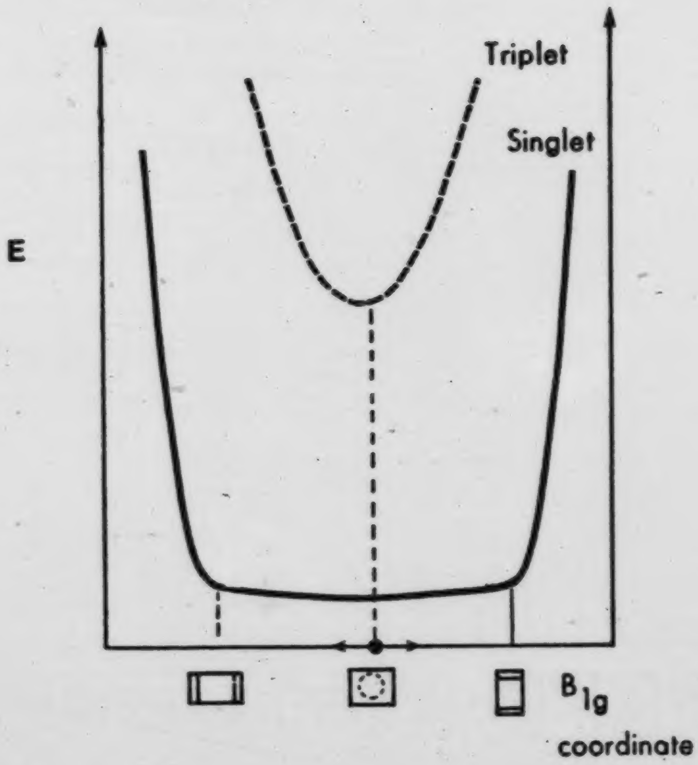
1973 Newton[19] (*ab initio* SCF, GVB 4-31G)
1975 Dewar[42] (MINDO-3)

FIGURE 10. Energy Profiles of the Lowest Singlet and Triplet States of Cyclobutadiene (Newton, *ab initio* SCF; Dewar, MINDO-3).

in an argon matrix. At 110°K, an interconversion with a 2.3 to 3.5-kcal/mol energy barrier should proceed efficiently and so the spectrum should be that of the species in the ground state.

A different rationalization of the existing infrared spectral evidence was proposed by Borden.[43] He argued that a square or "effectively square" singlet could be the ground state of cyclobutadiene since "repulsion between the two electrons in the non-bonding MO's of cyclobutadiene is minimized in a square geometry, resulting in a flat curve for rectangular distortion in the lowest singlet state." (Figure 11). He further added that a flat curve for distortion in this state (singlet) implied that its "stabilization by a pseudo-Jahn-Teller effect is not responsible for dropping its energy below that of the triplet state." It should be emphasized here that Borden's proposal is based solely on qualitative grounds, and a quantitative evaluation of the system is necessary.

From the foregoing discussion, it can be seen that if the ground state of cyclobutadiene had a geometry of lower symmetry than square, then all of the evidence, apart from the assignment of the infrared absorptions, would be mutually consistent. It became, therefore, necessary to undertake a detailed examination, both


Triplet
Singlet
E
B1g
coordinate

1975 Borden[43] (Qualitative CI)

FIGURE 11. Energy Profiles of the Lowest Singlet and Triplet States of Cyclobutadiene (Borden, Qualitative Configuration Interaction).

theoretical and experimental, of this system which could help to resolve the existing controversial problem. Experimentally, there was a definite need to closely re-examine the matrix-isolated species by vibrational spectroscopy. Theoretically, further refinement in the treatment of the system was eagerly awaited.

> "It always happens that when a man seizes
> upon an important idea, people inflamed
> with the same notion crop up all around."
>
> MARK TWAIN
>
> Life on the Mississippi

CHAPTER III

OUTLINE OF OBJECTIVES AND METHOD

The objective of this work was an examination of matrix-isolated cyclobutadiene (1) by vibrational spectroscopy in an attempt to elucidate the geometry of the ring. The method for the typical characterization of a matrix-isolated species by vibrational spectroscopy usually involves the steps schematically represented in Figure 12.[44] In theory, careful analysis of the vibrational spectra should distinguish between the two geometries, square and rectangular, which have been proposed for cyclobutadiene. The number and kinds of rotations and vibrations which will be infrared or Raman active (selection rules) can be predicted from symmetry considerations and depend upon the conformation assumed by the ring.[45] Of the 18 normal modes of vibration of 1 ($3n-6 = 18$), group theory predicts[45] that for square geometry (point group D_{4h}), four are infrared active and seven are Raman active, while for rectangular geometry (point group D_{2h}), seven are infrared active and nine are Raman active (Figures 13 and 14). Thus, if the bands in the spectra due to cyclobutadiene can be correctly identified, and if these bands can be rightly correlated to vibration types, then it should be possible to define the geometry of the ring.

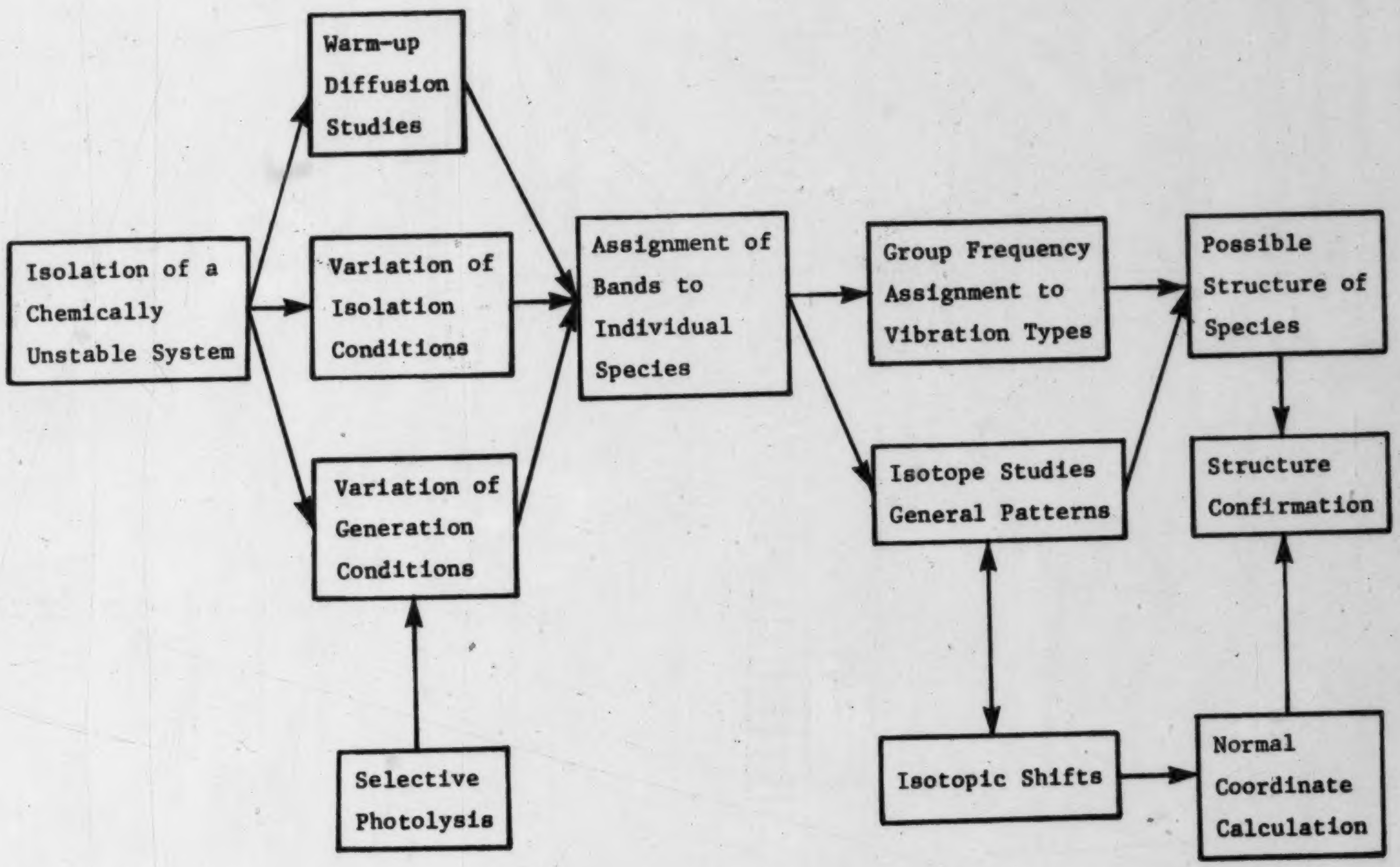

Isolation of a Chemically Unstable System
Warm-up Diffusion Studies
Variation of Isolation Conditions
Variation of Generation Conditions
Selective Photolysis
Assignment of Bands to Individual Species
Group Frequency Assignment to Vibration Types
Isotope Studies General Patterns
Isotopic Shifts
Possible Structure of Species
Structure Confirmation
Normal Coordinate Calculation

FIGURE 12.

Typical Characterization of a Matrix-Isolated Species by Vibrational Spectroscopy.[44]

RAMAN ACTIVE MODES

SQUARE TRIPLET

D_{4h}

ν_1 (A_{1g}), C-H Stretch

ν_2 (B_{1g}), C-H Stretch

ν_3 (A_{1g}), Symmetric ring breathing

ν_5 (B_{2g}), Asymmetric C-C stretch

ν_6 (B_{1g}), Asymmetric in-plane ring distortion

ν_7 (B_{2g}), Out-of-plane C-H wagging

ν_9 (E_g), Degenerate ring bend

RECTANGULAR SINGLET

D_{2h}

ν_1 (A_g), C-H Stretch (very strong)

ν_2 (B_{1g}), C-H Stretch

ν_3 (A_g), C=C Stretch (very strong)

ν_4 (A_g), In-plane CH bending

ν_5 (Ag), C-C Stretch (strong)

ν_6 (B_{1g}), In-plane CH bending

ν_7 (B_{2g}), Out-plane CH wagging

ν_8 (B_{3g}), Out-plane CH wagging

ν_9 (B_{1g}), C-C-C in-plane ring deformation

FIGURE 13. Raman Active Modes of Vibration of Square and Rectangular Cyclobutadiene.

INFRARED ACTIVE MODES

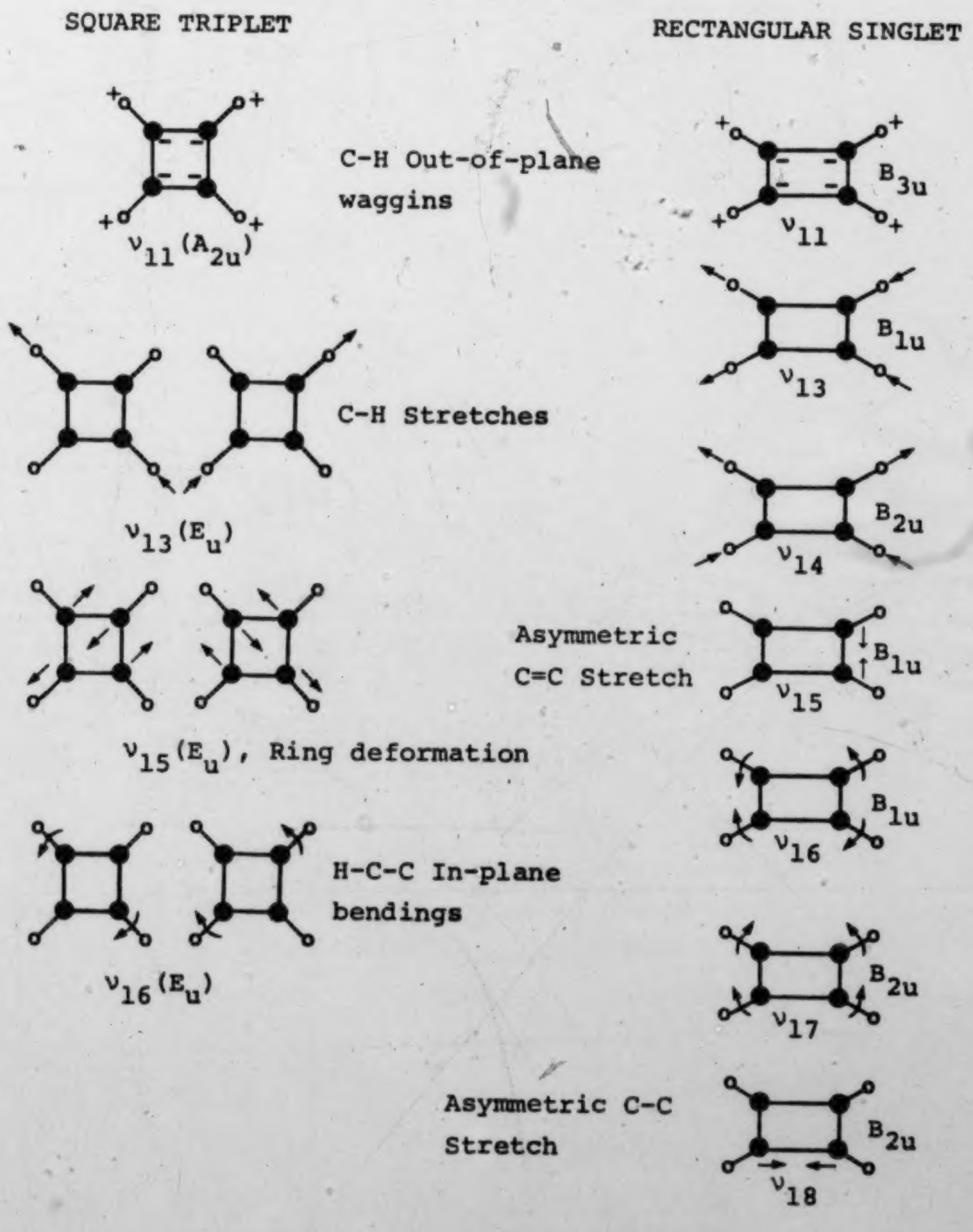

SQUARE TRIPLET
RECTANGULAR SINGLET
+
+
+
+
$\nu_{11}(A_{2u})$
C-H Out-of-plane waggins
B_{3u}
ν_{11}
B_{1u}
ν_{13}
C-H Stretches
$\nu_{13}(E_u)$
B_{2u}
ν_{14}
Asymmetric C=C Stretch
B_{1u}
ν_{15}
$\nu_{15}(E_u)$, Ring deformation
B_{1u}
ν_{16}
H-C-C In-plane bendings
$\nu_{16}(E_u)$
B_{2u}
ν_{17}
Asymmetric C-C Stretch
B_{2u}
ν_{18}

FIGURE 14. Infrared Active Modes of Vibration of Square and Rectangular Cyclobutadiene.

Since more than one product is formed from the photolysis of the precursors that yield cyclobutadiene, difficulties arise in the empirical assignment of individual infrared absorptions to a single species. There is a criterion which can be applied in the selection of bands attributable to cyclobutadiene i.e., all such bands should maintain the same relative intensity throughout the photolytic process, irrespective of matrix ratios, matrix materials and photoprecursors.[44] The destruction of the species by diffusion controlled dimerization ("warm-up diffusion studies") should also result in the disappearance of all selected bands, while during this warm-up process the same relative intensities are maintained. Thus, in order to identify all the absorption bands arising from one species, an accurate measurement of the intensities (optical densities) of the infrared absorptions is needed.[46]

After the absorptions in the infrared spectrum which satisfy the above conditions have been identified, the next task is to correlate the selected bands with the expected active modes of vibration of cyclobutadiene. This involves the use of the general correlations that have been established, chiefly for stable molecules, between the groups present in a molecule and the infrared bands observed in its spectrum.[45] Unfortunately, many reactive species (especially small molecules) have vibration frequencies that fall outside the "normal ranges", either because of their unique electronic structures or because of "coupling"[47] between interacting vibrational modes. Consequently, this so-called "Group Frequency Method" is the least rigorous method and is the most liable to error.

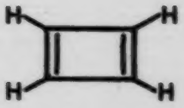
The use of isotopically substituted precursors is very useful in this respect. The species thus generated have different vibration frequencies.[48] The magnitudes of these shifts show which atoms are principally involved in each vibration. Thus, it is often possible to identify unambigously many observed infrared bands on the basis of their shifts in the spectra of the appropriately labelled molecules. The method is considered to be most useful for small species (e.g., cyclobutadiene) where any isotopic change alters all vibrations detectably. Substitution of hydrogen by either tritium or deuterium constitutes an ideal case since the change in the corresponding reduced masses is maximum and the isotopic shifts involved are consequently very large (Figure 15).

$$\frac{\nu^{i}}{\nu^{H}} = \left(\frac{\mu}{\mu^{i}}\right)^{1/2}, \qquad \frac{\nu^{D}}{\nu^{H}} = \left(\frac{M+2}{2M+2}\right)^{1/2}$$

$$\frac{\nu^{T}}{\nu^{H}} = \left(\frac{M+3}{3M+3}\right)^{1/2}$$

FIGURE 15. Ratio Between the Diatomic R-D or R-T Stretching Frequency and that of the R-H Oscillator (see Chapter IV in reference 48).

In the case of cyclobutadiene (1), examination first of the fully deuterated species 28 provides information which is more readily interpreted than that from partially substituted species. Partial isotopic substitution destroys the symmetry of the ring (Figure 16), so that different selection rules[45] apply to the prediction of the allowed fundamental vibrations.



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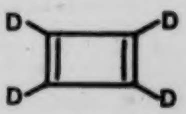

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"Normal Coordinate Analysis"[45,57] allows a more definite assignment of all of the observed infrared bands to the expected normal modes of vibration of the molecule. However, the calculation of frequencies by this analysis is, in practice, applicable only after the spectrum of the particular species has been largely identified. Nevertheless, in certain instances it may be helpful in suggesting frequencies for bands that have not yet been observed or conclusively identified. Again, one important source of data is provided by the spectra of fully isotopically substituted molecules.[48] It has been suggested[44] that perhaps the most satisfactory use of normal coordinate analysis is for the explanation of "anomalous" isotope effects.

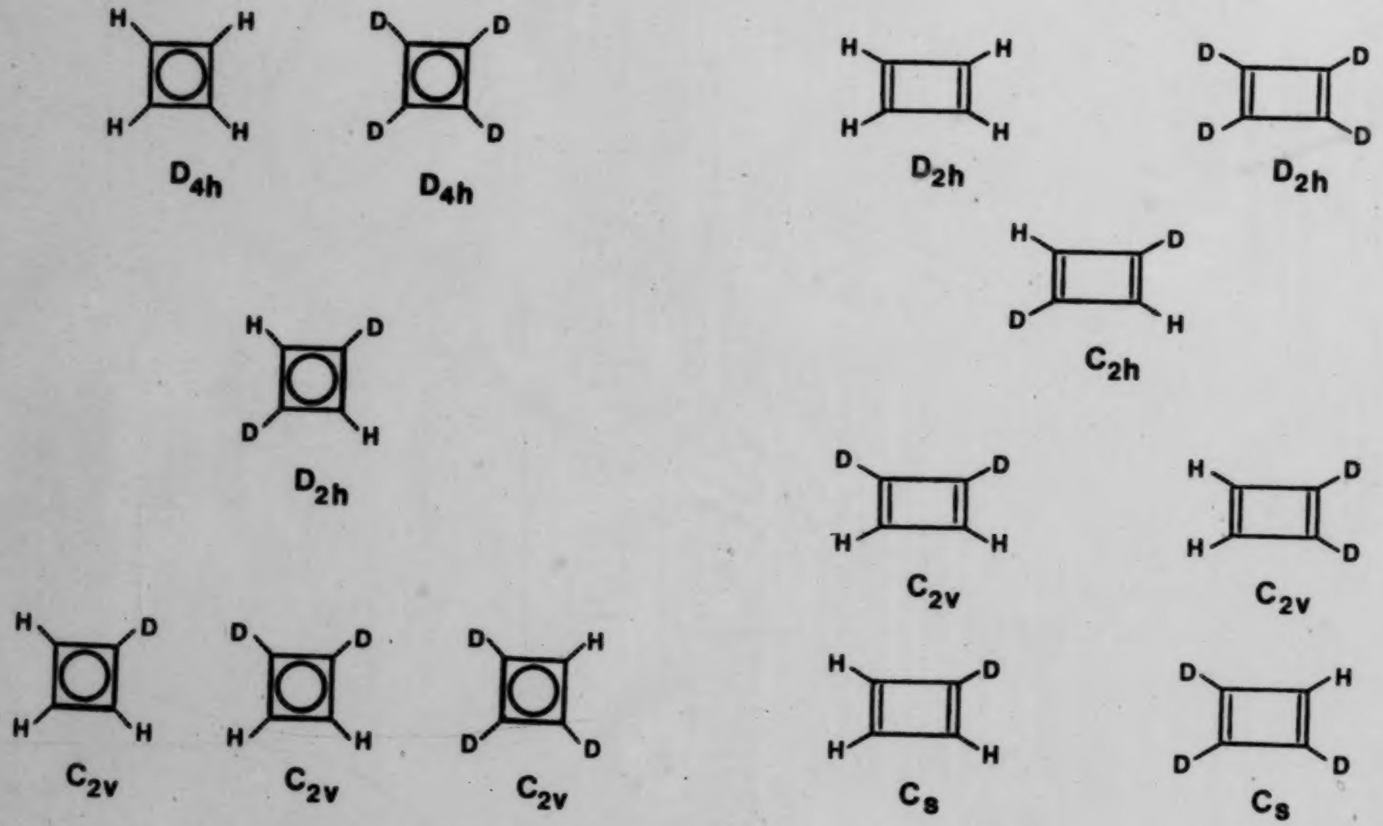

D$_{4h}$
D$_{4h}$
D$_{2h}$
D$_{2h}$
C$_{2h}$
D$_{2h}$
C$_{2v}$
C$_{2v}$
C$_{2v}$
C$_{2v}$
C$_{2v}$
C$_s$
C$_s$

FIGURE 16. Symmetry Assignment of Square and Rectangular Cyclobutadiene and the Corresponding Deuterated Analogues.

The isotopic substitution of one atom may affect more than one vibration frequency. If several vibrations of the same symmetry lie close together in energy, there may well be considerable "mixing" between them.[45b,c] This will be reflected in a sharing of the expected isotope shifts between all the bands and should be reproduced in the normal coordinate calculations. The extent of the mixing of the ideal modes of vibration can then be calculated.

The study of vibrations that for symmetry reasons do not give rise to infrared bands can be undertaken by Raman spectroscopy.[49] The frequencies of such vibrations have often been found to be extremely useful in normal coordinate analysis.

"Look for the stars, you'll say that there are none;
Look for a second time, and, one by one,
You mark them twinkling out with silvery light
And wonder how they could elude the sight!"

WILLIAM WORDSWORTH
Calm is the Fragrant Air

The following abbreviations are used for chemical names.

HMPA, hexamethylphosphoric triamide

MClPBA, *m*-chloroperbenzoic acid

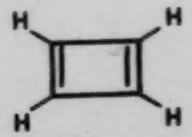
THF, tetrahydrofuran

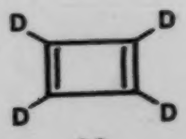
TsCl, *p*-toluenesulfonyl chloride

CHAPTER IV

RESULTS AND DISCUSSION

The infrared spectra of matrix-isolated cyclobutadiene (1) and its fully deuterated isotopic analogue (28) have been recorded and analyzed. Since the use of


1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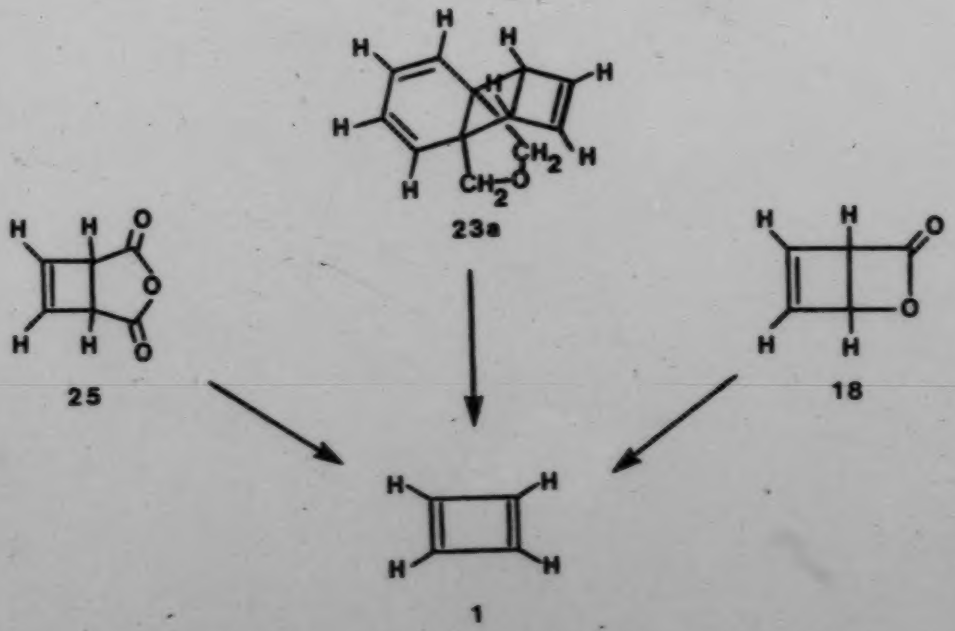
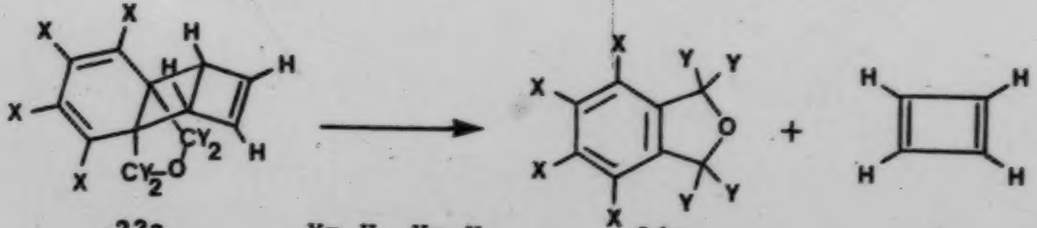
only one precursor for the photochemical generation of matrix-isolated cyclobutadiene may lead to a mis-interpretation of the observed spectra (see Chapter II, section 2.2), the characterization of photolysates arising from several different precursors was warranted. The

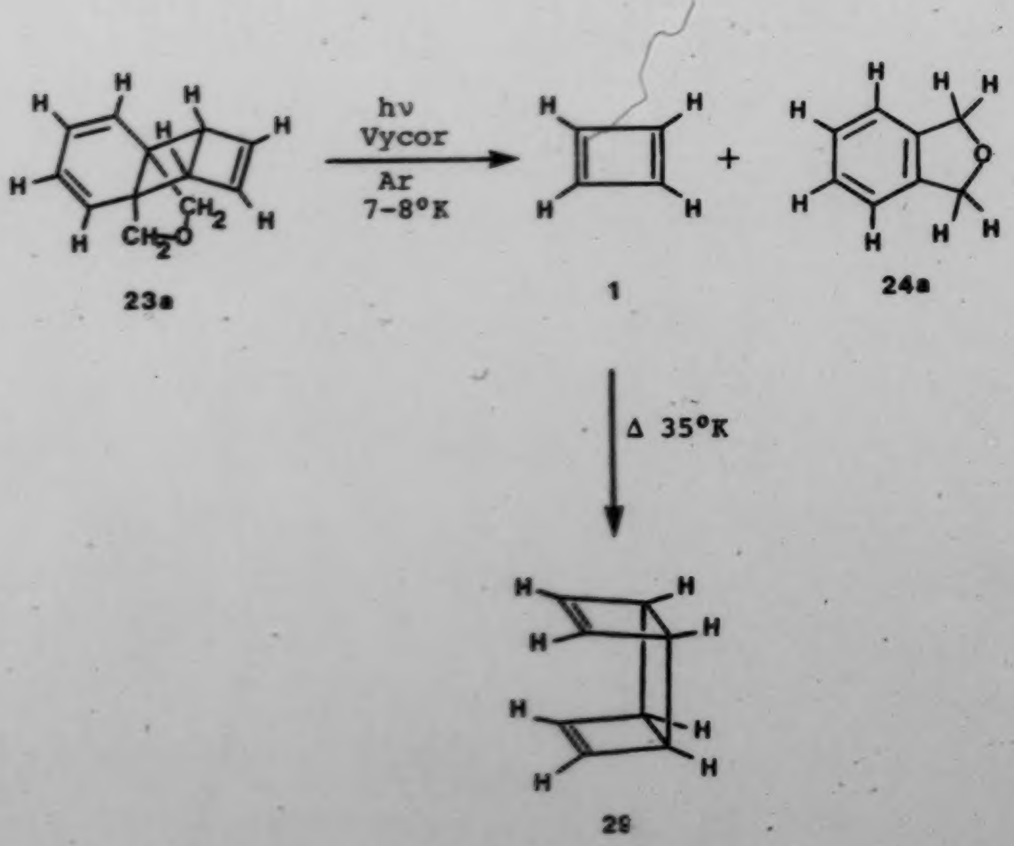


precursors utilized to produce **1** were the tetracyclic ether **23a**,[34] photo-α-pyrone (**18**),[35,36] and cyclobutene-dicarboxylic anhydride (**25**).[38] These are the only known photoprecursors capable of yielding the desired species with reasonable efficiency. Of these three precursors, the photocleavage of the tetracyclic ether **23a** in rare gas matrices proceeds most efficiently to provide the highest concentration of cyclobutadiene, but the concurrent generation of phthalan (**24a**) masks several regions of the infrared spectrum. However, introduction of deuterium isotopic substitution in **23a**, as indicated in **23b-d**, shifts the infrared absorptions of the phthalan **24a** to those of **24b-d**. This permits inspection of the vibrational modes of **1** in the entire region from 4000 to 400 cm^{-1}.



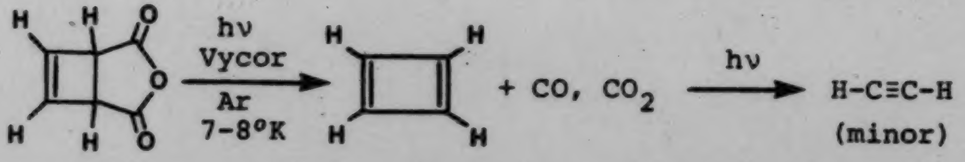
23a	X= H, Y= H	**24a**	**1**
23b	X= D, Y= H	**24b**	
23c	X= H, Y= D	**24c**	
23d	X= D, Y= D	**24d**	

The infrared spectrum of the photolysate of the matrix-isolated (Ar, 16-18°K) tetracyclic ether 23a[50] on irradiation (7-8°K) with two Hanovia medium pressure mercury lamps (140 W, Vycor filters) was recorded with a Nicolet 7199 FT-IR Spectrophotometer (0.5 cm^{-1} resolution, 100-500 interferograms averaged). There were observed the two previously reported bands at 1240 and 572 cm^{-1}.[35,36,38,39] In addition, only with the use of the above spectrophotometer, two weak absorptions at 1523 and 723 cm^{-1} that had escaped earlier notice[38,39] were detected for the first time. All four absorptions in-



creased in intensity upon photolysis, and upon warming the argon matrix to 35°K, they decreased and were replaced by those of the *syn*-dimer of **1** (**29**).[51] The bands also kept the same relative intensity throughout these processes, and therefore it was highly likely that they were attributable to cyclobutadiene. The presence of these absorptions in the spectra of photolysates arising from the other two precursors, **18** and **25**, was subsequently confirmed.

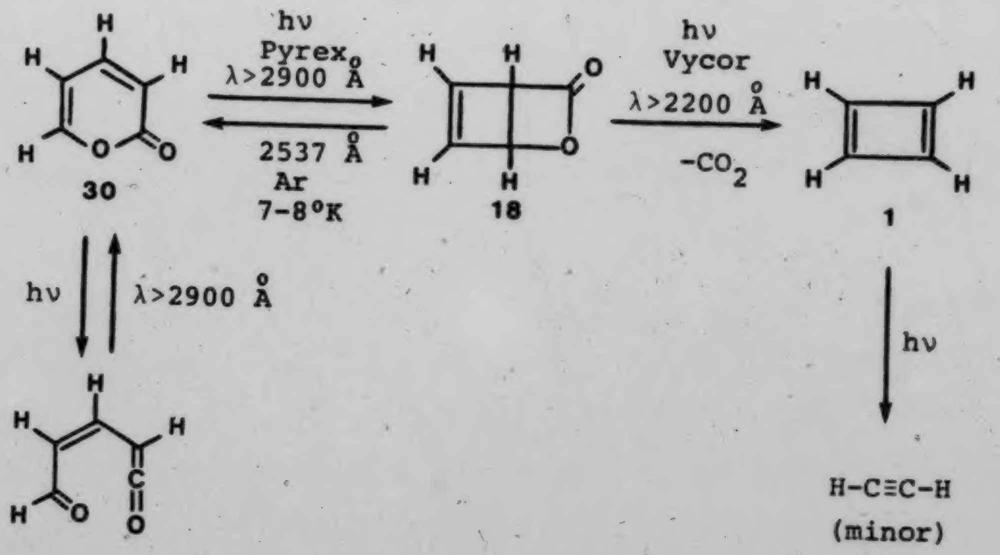
Photocleavage (7-8°K) of matrix-isolated (Ar, 15-17°K) cyclobutenedicarboxylic anhydride (**25**)[52] with two medium pressure mercury lamps (140 W, 10-12 h) through Vycor filters resulted in a relatively clean conversion to cyclobutadiene. The spectra of the photolysate recorded with the Nicolet Interferometer exhibited



25 **1**

the following absorptions consisting of four doublets: 1530, 1527-1528; 1245, 1242; 721, 718; and 591, 576 cm^{-1}. These doublets correspond to the bands at 1523, 1240, 723 and 572 cm^{-1} previously detected from the photolysate of **23a**.

Photo-α-pyrone (18)[31] was cleanly prepared by irradiation (7-8°K, 20 h) of matrix-isolated (Argon, 10-15°K) α-pyrone (30)[53] with two medium pressure mercury lamps (140 W) through a Pyrex filter. The desired photofragmentation to cyclobutadiene was accomplished



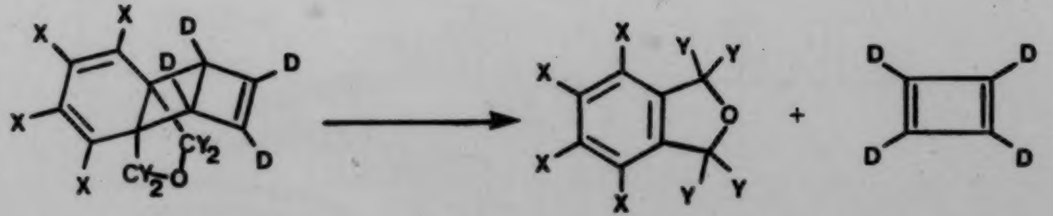
by continuing the irradiation (7-12 h) through Vycor filters. This converted any remaining α-pyrone into photo-α-pyrone and also cleaved the latter to cyclobutadiene. In this way acetylene, the photoproduct of cyclobutadiene, formed only as a very minor by-product. The infrared spectra (Nicolet Interferometer) showed absorptions at 1531, 1529; 1244, 1241; 721, 719; and 576, 574 cm^{-1}, each pair (doublet) again corresponding to the four previously detected bands, respectively.

The four absorptions at 1523, 1240, 723 and 572 cm^{-1}, observed in the spectrum of the photolysate from 23a and tentatively assigned to 1, were therefore also observed in the spectra from the products of the other two precursors. However, each absorption of the photoproducts derived from the precursors which generate CO_2 upon photolysis appears as a doublet. This effect is quite likely due to the interaction of CO_2 with cyclobutadiene since both species are trapped in the site occupied by the precursor.

The four lines maintained approximately the same relative intensity irrespective of the photoprecursor used and all behaved similarly upon photolysis and warm-up. This behaviour constitutes convincing evidence for their assignment to a single reactive species, 1, and thus, our initial tentative assignment was confirmed.

A decision about the structure of cyclobutadiene had to await the outcome of the symmetry assignment of the four observed vibrations. The most informative and reliable method for assignment of the observed bands to the expected normal modes of vibration of 1 involves the use of deuterium isotopic substitution (see Chapter III). The isotope shifts would indicate whether the band at 1240 cm^{-1} is due mainly to a skeletal vibration in a square structure, as suggested by Krantz,[19] or to a H-C-C in-plane bending motion. Further, the band at

1523 cm^{-1} is very likely due to a C=C stretching vibration of the ring and should shift accordinly upon deuteration. The expected isotope shift, if observed, would confirm this assignment and exclude the possibility of a square conformation for 1. Since partial isotopic substitution destroys the symmetry of the ring (p. 51), our first task was the infrared spectral characterization of the unknown cyclobutadiene-d_4 (28). For this purpose, we generated the species from the tetracyclic ether 31a (for the synthesis of 31a, see the scheme outlined in Figure 17). However, photolysis of this compound isolated in an argon matrix proved rather disappointing since all of the infrared bands of 28 (*vide infra*) appeared to be masked by those of the concomitant



31a	X= H, Y= H	**24a**	**28**
31b	X= D, Y= H	**24b**	
31c	X= H, Y= D	**24c**	
31d	X= D, Y= D	**24d**	

phthalan 24a. The major features of the spectrum were

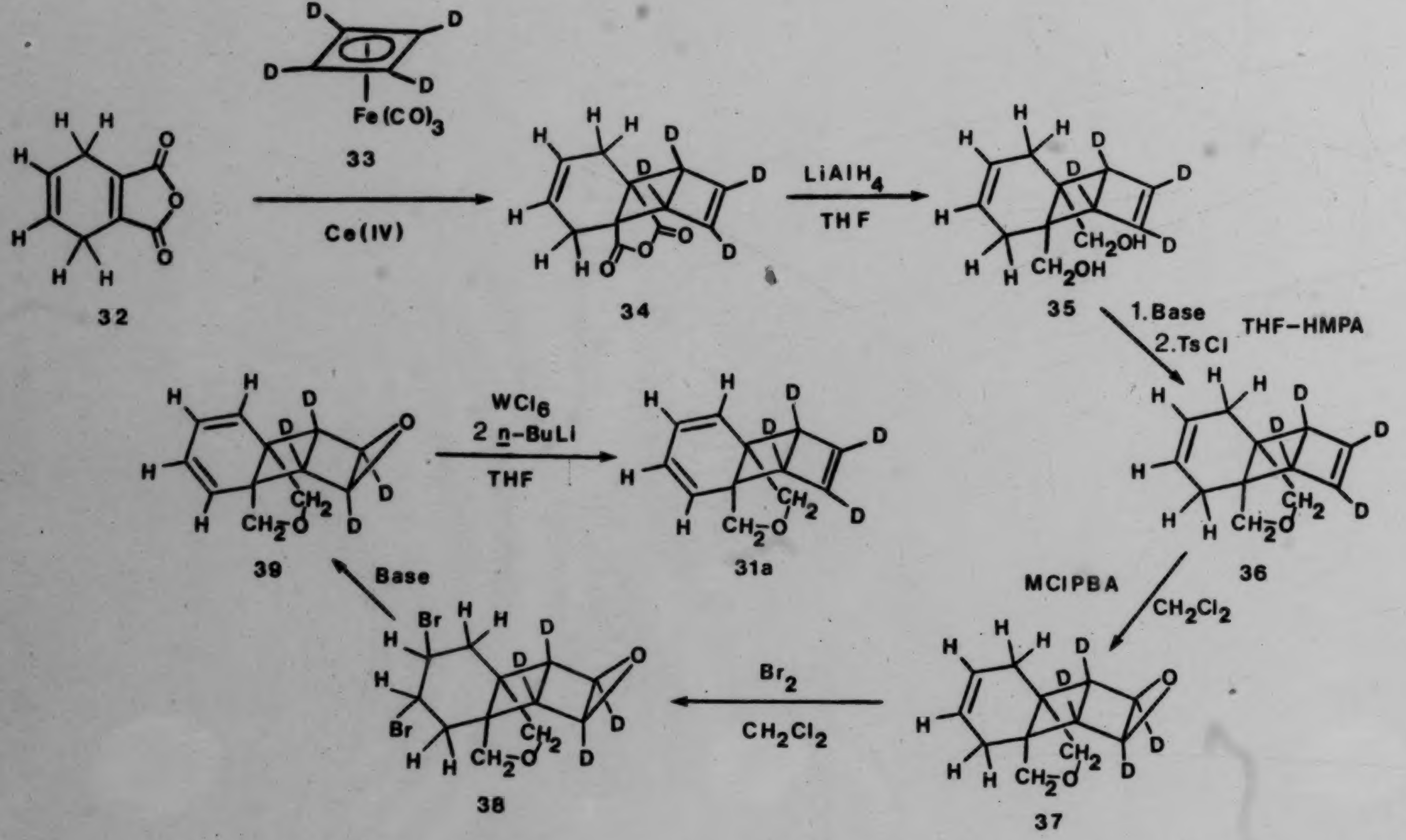
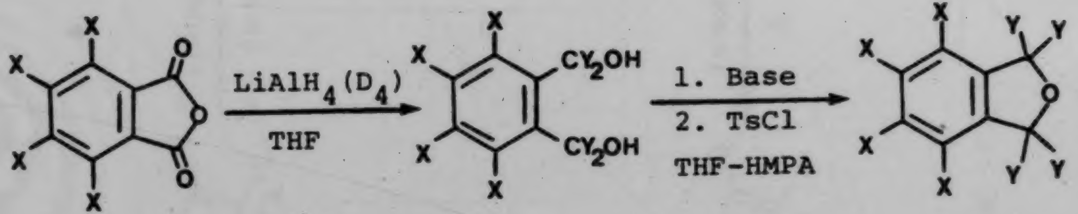

32
33
$Fe(CO)_3$
Ce(IV)
34
$LiAlH_4$
THF
35
1.Base
2.TsCl
THF–HMPA
36
MClPBA
CH_2Cl_2
37
Br_2
CH_2Cl_2
38
Base
39
WCl_6
2 n-BuLi
THF
31a

FIGURE 17. Synthetic Scheme for the Preparation of 31a.[50]

two strong shoulders at around 1040 and 420 cm^{-1}. Introduction of deuterium isotopic substitution in the phathalan **24a** shifts its infrared absorptions to those of **24b-d**. This would permit examination of the regions masked by **24a**. The synthesis of the isotopically substituted phthalans **24a-d** allowed recording of their in-



40a X= H
40b X= D

41a	X= H, Y= H	**24a**
41b	X= D, Y= H	**24b**
41c	X= H, Y= D	**24c**
41d	X= D, Y= D	**24d**

frared spectra in argon matrices at either 4.2 or 10°K and at 35°K. From all of these spectra it was possible to conclude that the best precursor for the confirmatory observation of the features already hinted at for cyclobutadiene-d_4 (**28**) was **31b** (Figure 18). This tetracyclic ether was co-condensed (15-18°K) with an excess of argon (1:100-500), and the resulting transparent matrix was photolyzed (7-8°K) with two medium pressure mercury lamps (140 W, Vycor filters). The infrared spectra of the photolysate recorded with the Nicolet FT-IR Inter-

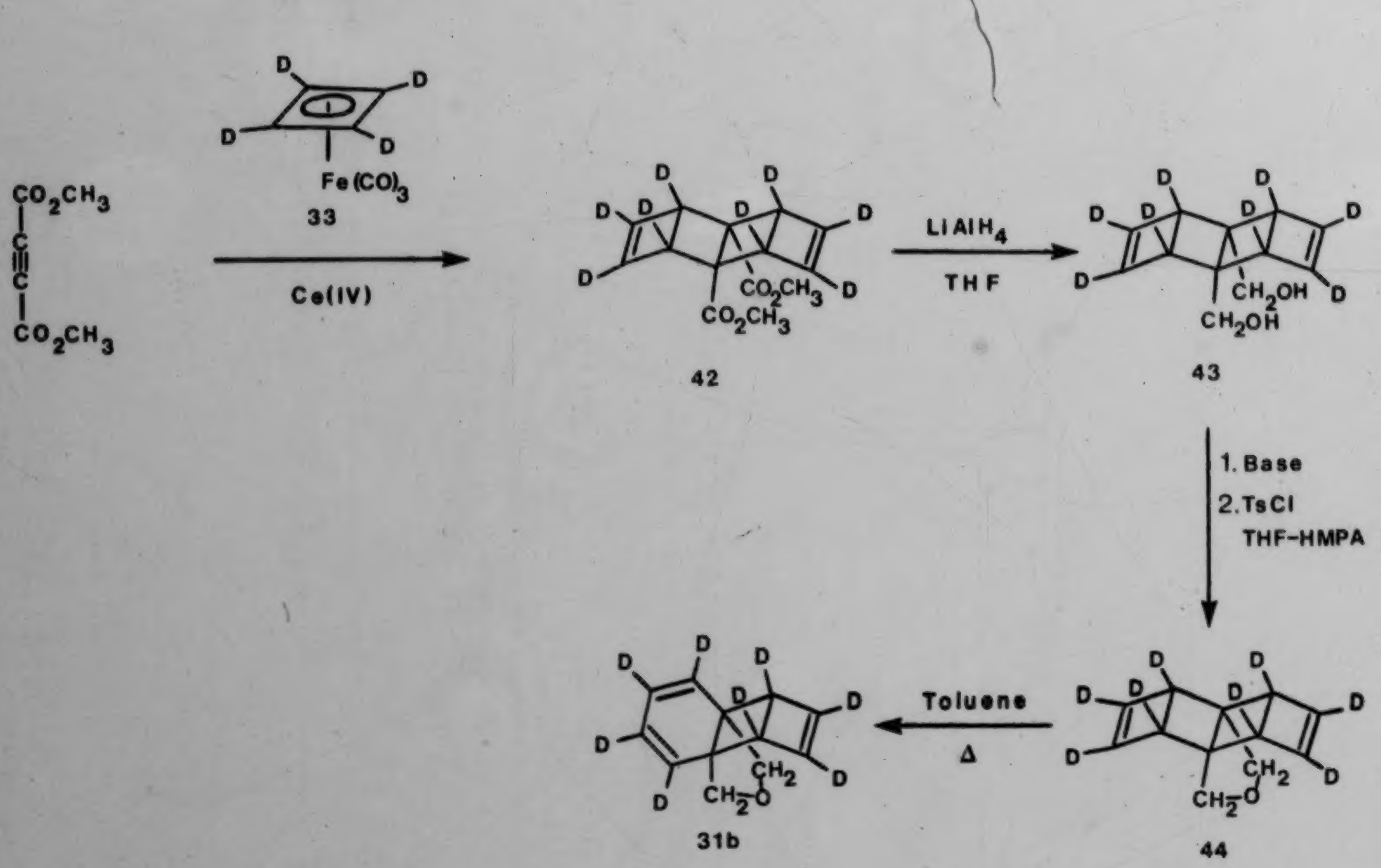
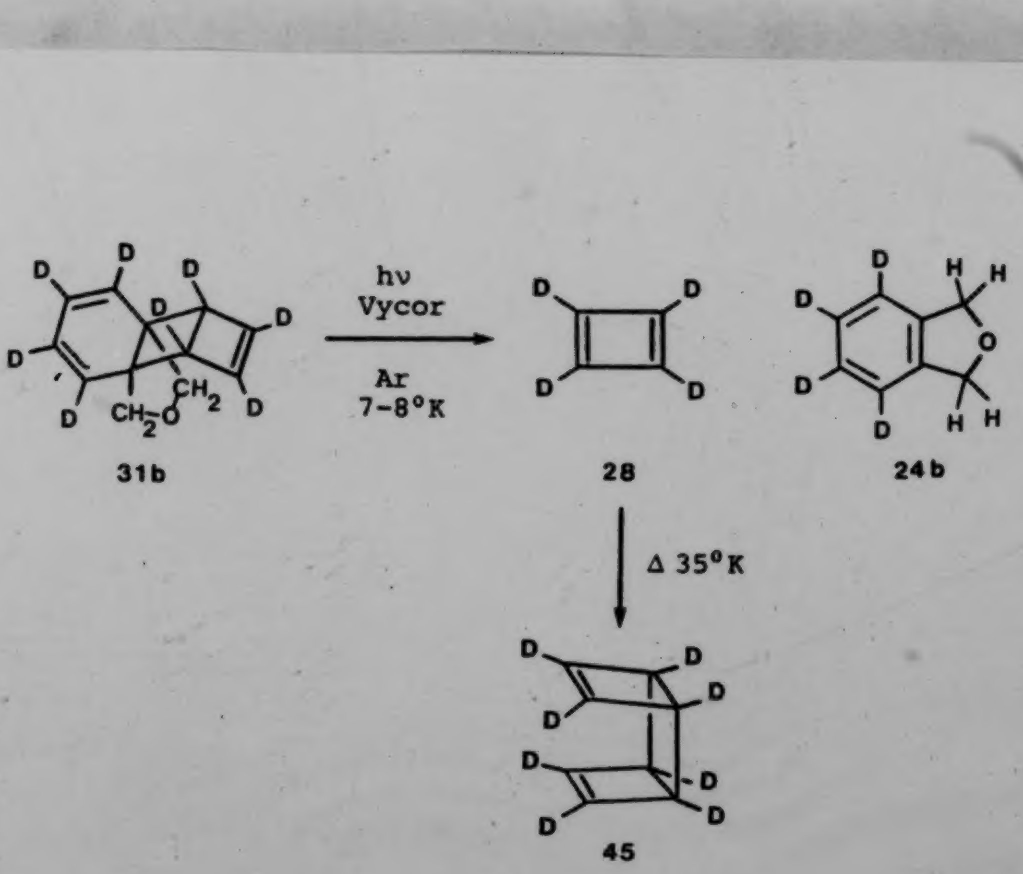
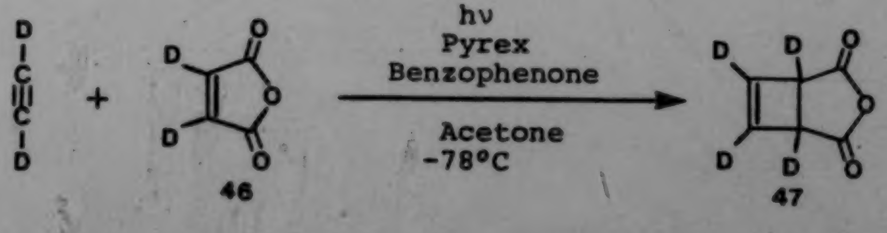

33
Ce(IV)
42
LiAlH$_4$
THF
43
1. Base
2. TsCl
THF-HMPA
44
Toluene
Δ
31b

FIGURE 18. Synthesis of 31b.[54]

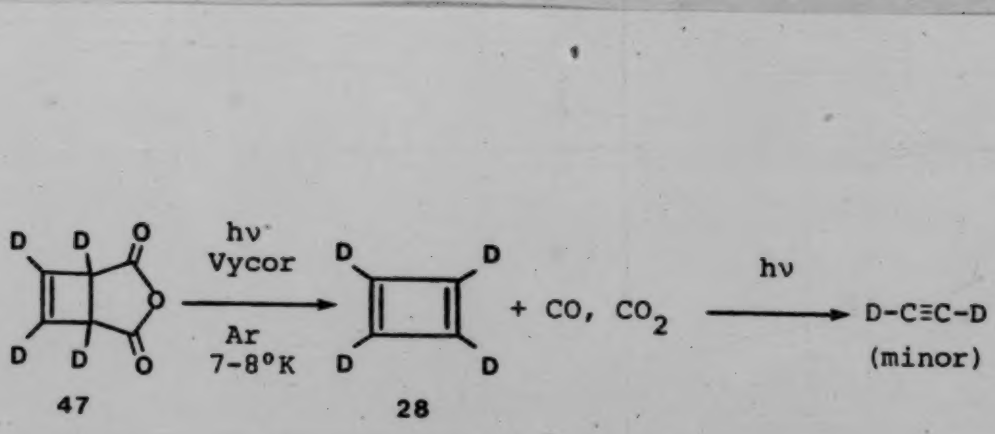

hν
Vycor
Ar
7-8°K
Δ 35°K
31b
28
24b
45

ferometer revealed absorptions at 1456, 1043, 609 and 421 cm^{-1}. The intensity of these absorptions changed during photolysis and warm-up in a manner similar to the bands ascribed to the per-protio counterpart. The presence of these bands in the spectra of the photolysates arising from the other two fully deuterated precursors was also confirmed.

Cyclobutenedicarboxylic anhydride-$\underline{d}_4$ (47) was prepared by benzophenone-sensitized photoaddition of acetylene-$\underline{d}_2$[55]

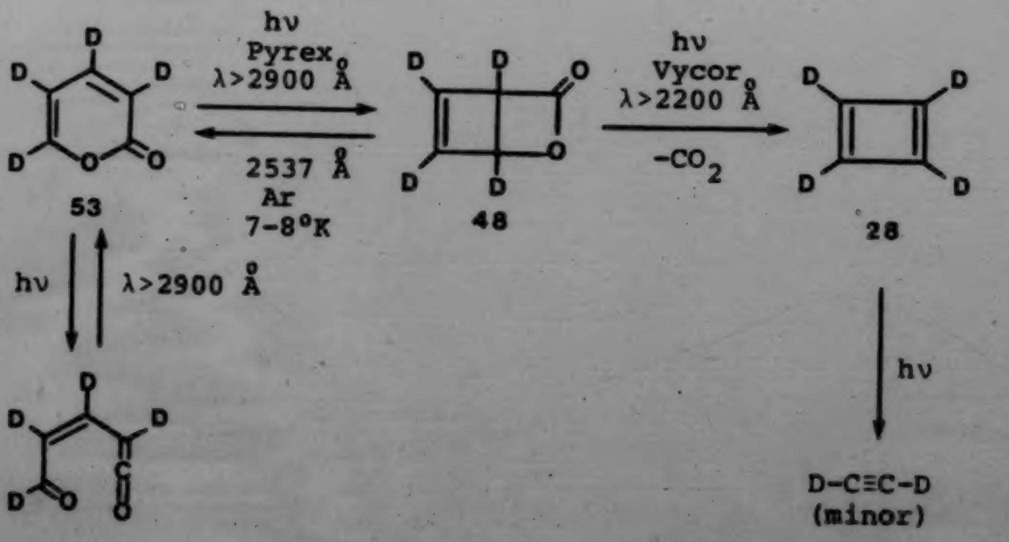

hν
Pyrex
Benzophenone
Acetone
-78°C
46
47

and maleic anhydride-$\underline{d}_2$ (46)[56] in the same manner as described for the known per-protio compound.[52] Photolysis


hν
Vycor
Ar
7-8°K
+ CO, CO2
hν
D-C≡C-D
(minor)
47
28

(7-8°K, 12-15 h) of **47** isolated in an argon matrix (15-17°K) gave a clean conversion to cyclobutadiene-*d*$_4$. The ir spectra of the photolysate exhibited absorptions at 1464, 1460; 1046, 1044; 609, 608; and 432, 425 cm^{-1}, corresponding to the four bands detected from the ether **31b** but again split into doublets.

Photo-α-pyrone-*d*$_4$ (**48**) was prepared *in situ* from α-pyrone-*d*$_4$ (Figure 19) in the same manner as the per-protio analogue (*vide supra*). Upon photocleavage of this lactone to cyclobutadiene-*d*$_4$, the spectra showed absorptions (doublets) at 1455, 1450; 1047, 1044; 609, 608; and 426, 423 cm^{-1}, in full agreement with the data obtained from the


hν
Pyrex
λ>2900 Å
2537 Å
Ar
7-8°K
hν
Vycor
λ>2200 Å
-CO2
hν
λ>2900 Å
hν
D-C≡C-D
(minor)
53
48
28

other two precursors.

Table 3 summarizes all the infrared data gathered during the course of this research. In an attempt to observe any bands, thus far undetected, which could be attributable to cyclobutadiene, we also examined the photolysate arising from the tetracyclic ether 23d (Figure 20). No additional information could be obtained from the corresponding infrared spectra.

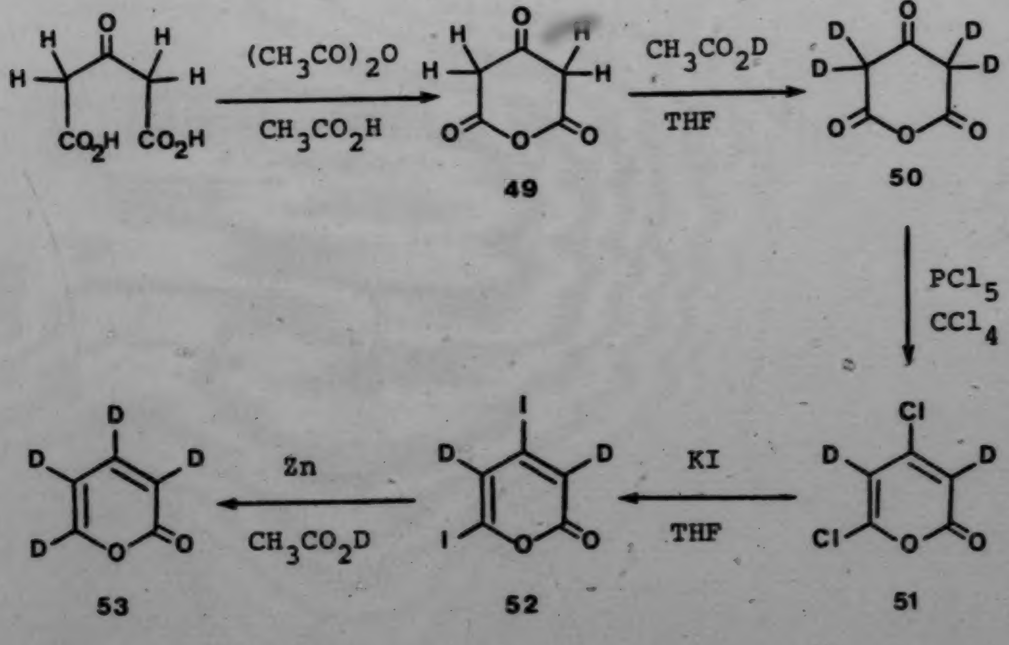

(CH3CO)2O
CH3CO2H
49
CH3CO2D
THF
50
PCl5
CCl4
51
KI
THF
52
Zn
CH3CO2D
53

FIGURE 19. Synthetic Scheme for α-Pyrone-d_4 (53).

C_4H_4(1)				C_4D_4(28)			
Precursor	Band	Wave Number (cm^{-1})	Relative Intensity[a]	Precursor	Band	Wave Number (cm^{-1})	Relative Intensity[a]
23(a,d)	A	1523	1.4	31(a,b)	A'	1456	2.9
	B	1240	41.1		B'	1043	21.0
	C	723	12.4		C'	609	16.2
	D	572	100.0		D'	421	100.0
25	A	1527-28, 1530	2.2	47	A'	1460, 1464	3.6
	B	1242, 1245	38.9		B'	1044, 1046	20.3
	C	718, 721	9.0		C'	608, 609	27.8
	D	576, 591	100.0		D'	425, 432	100.0
18	A	1529, 1531	1.4	48	A'	1450, 1455	2.5
	B	1241, 1244	35.0		B'	1044, 1047	21.8
	C	719, 721	6.8		C'	608, 609	20.4
	D	574, 576	100.0		D'	423, 426	100.0

[a] Relative integrated absorbances of the bands averaged over several runs.

TABLE 3. Infrared Absorptions of C_4H_4(1) and C_4D_4(28).

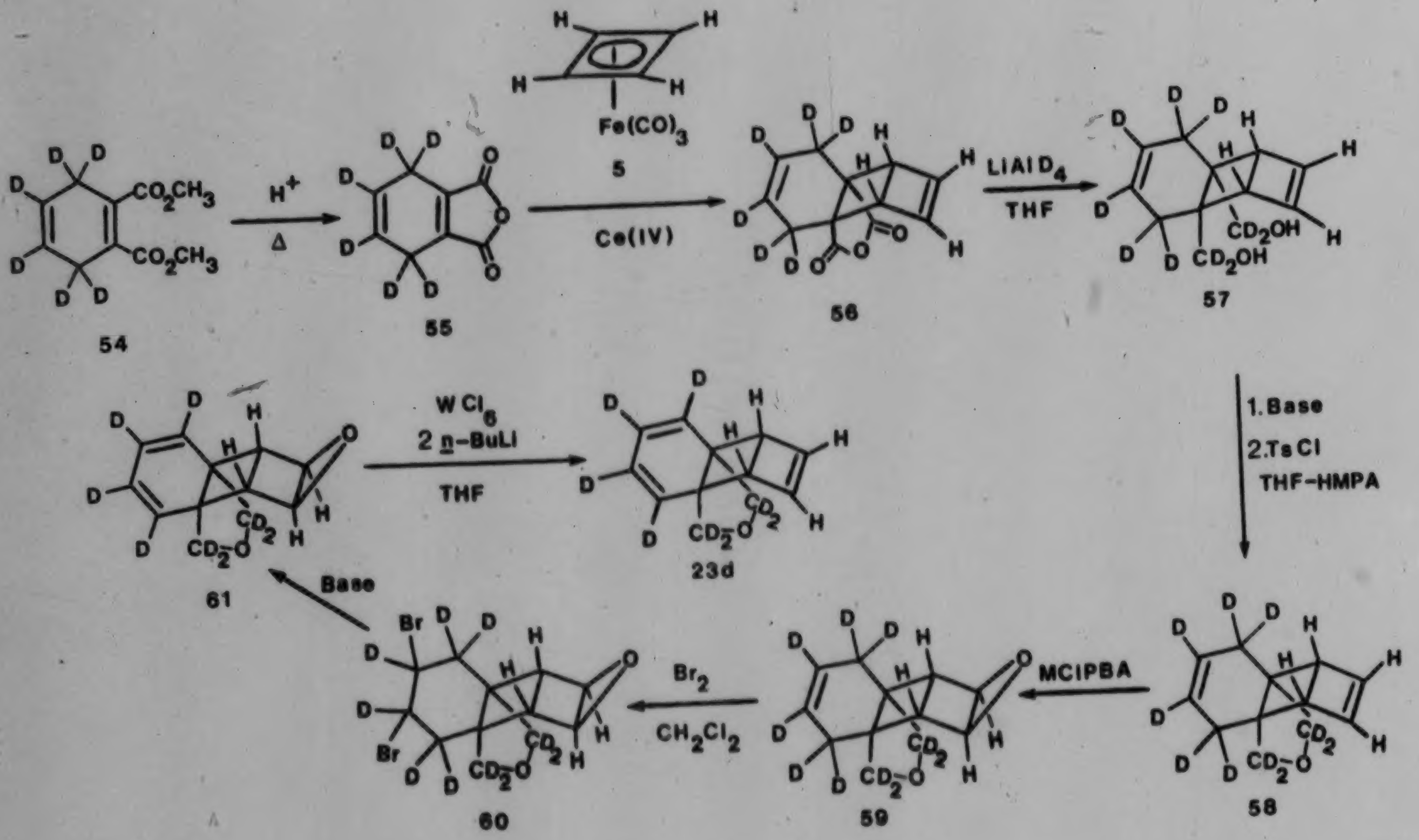

54
H+
Δ
55
Fe(CO)3
5
Ce(IV)
56
LiAlD4
THF
57
1.Base
2.TsCl
THF-HMPA
58
MCIPBA
59
Br2
CH2Cl2
60
Base
61
WCl6
2 n-BuLi
THF
23d

FIGURE 20. Synthetic Scheme for 23d.[50]

DISCUSSION

The spectral data presented (Table 3) exclude the possibility of cyclobutadiene (**1**) possessing square geometry (point group D_{4h}). The appearance of four absorptions below 2000 cm^{-1} removes this possibility since group theory (*vide supra*) predicts for this symmetry only three infrared-active vibrations in addition to the C-H stretching vibration which should appear around 3000 cm^{-1}. The band at 1523 cm^{-1} (**A**) which shifts to 1456 cm^{-1} (**A'**) upon deuteration is undoubtedly due to the C=C stretching vibration of **1** and supports the above conclusion.

On the other hand, the spectral evidence is consistent with a rectangular geometry for cyclobutadiene, point group D_{2h}. The application of the "product rule"[57] to the present data leads to the following symmetry assignment[58] of the vibrations **A**-**D** and **A'**-**D'** (Table 3). The pairs of vibrations **B** and **C** and **B'** and **C'** have the same symmetry, designated herein as B_{2u} (product rule ratio: theoretical 1.927, observed 1.918 where the C-H and C-D stretching frequencies are assumed to have the harmonic ratio 1.363); **D** and **D'** are the sole B_{3u} out-of-plane hydrogen and deuterium bending vibrations (product rule ratio: theoretical 1.363, observed 1.357); and finally the C=C stretching vibrations, **A** and **A'**, and unobserved vibrations (*vide infra*) that correspond primarily to H-C-C and D-C-C bending motions, have B_{1u} symmetry.

The isotope shifts indicate that **B** (1240 cm^{-1}) is due largely to the H-C-C in-plane bending vibration, and not primarily to the C-C stretching motion which contributes mainly to **C** (723 cm^{-1}). In the fully deuterated species the vibrations **B'** and **C'** (1043 and 609 cm^{-1}) are both heavy mixtures of these two coupled motions. Therefore, the assignment of **B** (1240 cm^{-1}) primarily to a C-C stretching vibration is definitely inconsistent with the isotope shifts, and the conclusion arrived at earlier by Krantz[19,41] completely loses its ground.

A reasonable set of force constants reproduced the observed frequencies well through a GF normal coordinate calculation,[57] which was kindly performed by Professor J.E. Bertie of this Department (Table 4). The fact that the observed frequencies were reproduced using a reasonable set of parameters provides support for the assumed rectangular geometry and also for the symmetry assignments.

We have already noted (*vide supra*) that the in-plane H-C=C bending vibration of B_{1u} symmetry is not observed. Although some very weak absorptions at around 950 cm^{-1} in the case of **1**, and around 750 cm^{-1} in the case of the per-deutero species **28**, are present in the spectra, their

	C_4H_4			C_4D_4	
	Calculated	Observed		Calculated	Observed
B_{1u}	1540	1523	B_{1u}	1455	1456
B_{1u}	974	-	B_{1u}	713	-
B_{2u}	1223	1240	B_{2u}	1054	1043
B_{2u}	740	723	B_{2u}	604	609
B_{3u}	574	572	B_{3u}	422	421

Internal coordinates: 4 C-H, 2 C=C, 2 C-C, 4 H-C-C, 4 H-C=C, 4 out-of-plane $H-C=C_2$.

Geometry assumed: $r_{C=C} = 1.37$ Å, $r_{C-C} = 1.51$ Å, $r_{C-H} = 1.08$ Å, H-C-C = 135°.

Force constants: C-H, 4.85; C=C, 7.425; C-C, 2.55 (all mdyne Å^{-1}); H-C-C and H-C=C, 0.367 mdyne Å; out-of-plane $H-C-C_2$, 0.2105 mdyne Å; all interaction force constants 0.0.

TABLE 4. Observed and Calculated Frequencies for C_4H_4 (1) and C_4D_4 (28).

intensities are too small to be confirmed with the precursors, the spectroscopic method, and the sophistication of instrumentation used for this study.

The spectral data presented above clearly disprove the previous conclusion that the ring in cyclobutadiene is square. These experimental observations have been corroborated by recent theoretical treatments. Ab initio calculations on both the SCF level and with electronic correlation (CI) have been reported by Kollmar and Staemmler[59] (whose report appeared during our study) and by Borden, Davidson and Hart[60] (whose report appeared this year). These can be viewed as further refinements of the earlier work of Buenker and Peyerimhoff[18] and of Allinger[15b] (Table 5). For square geometry, the singlet (SS) has been found to be more stable than the triplet (ST) by either 7 kcal/mol (Kollmar-Staemmler) or 18 kcal/mol (Borden-Davidson-Hart). This violation of Hund's rule has been explained as "an effect of dynamic spin polarization."[*] Also, distortion of the square geometry

---

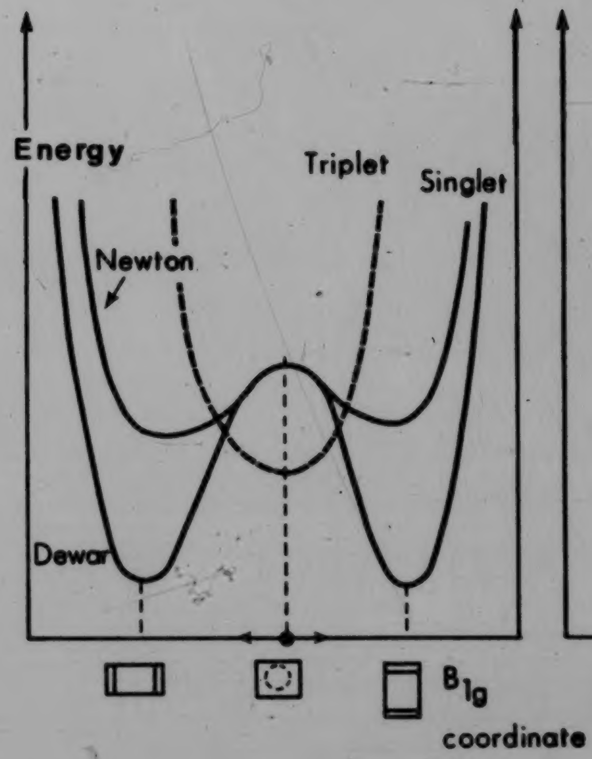
[*] Electron correlation within the π system lowers the energy of the singlet more than that of the triplet.[18] The reason for this extra stabilization of the singlet is what has been called by Kollmar and Staemmler[59] "a dynamic spin polarization."

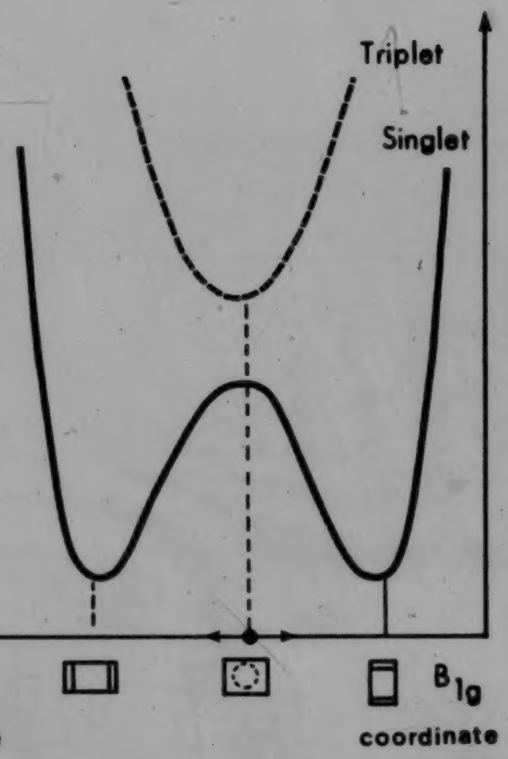
	SS	ST	RS
ALLINGER (1968) SCF PP	23	0	6
BUENKER-PEYERIMHOFF (1968) *ab initio* SCF, extended CI	-14	0	-24
ALLINGER (1968) SCF PP, doubly excited CI	-10	0	-15
NEWTON (1973)			
ab initio SCF	-	0	-
GVB	8	0	0<RS<8
DEWAR (1975) MINDO-3	7	0	- 6
KOLLMAR-STAEMMLER (1977) *ab initio* SCF, σ-space CI	- 7	0	-21
BORDEN-DAVIDSON-HART (1978) *ab initio* SCF, σ- and π-space CI	-14 to -18	0	-22 to -26

TABLE 5. Calculated Relative Energies (kcal/mol) of Square Singlet (SS) and Triplet (ST) and Rectangular Singlet (RS) Cyclobutadiene.

to a rectangular structure has been found[60] to stabilize the singlet state further (pseudo-Jahn-Teller effect),[11] corroborating Snyder's[12] earlier finding. The energy difference between the rectangular minimum (RS) and the square (SS) conformations of singlet cyclobutadiene has now been estimated to be between 4.2-8.3 kcal/mol (Borden-Davidson-Hart) and 14 kcal/mol (Kollmar-Staemmler). As a result, both groups of workers have concluded that a rectangular singlet (RS) represents the ground state of **1** (Table 5 and Figure 21).

The evidence, both theoretical and experimental, is therefore only consistent with a geometry less symmetrical than D_{4h}, very likely rectangular. Although the present study does not define the exact symmetry of the molecule, at minimum it provides a solution to the recent controversial cyclobutadiene problem. Thus, the chemistry of this system, derivatives and parent species, is now mutually consistent.


Energy
Triplet
Singlet
Newton
Dewar
B_{1g}
coordinate


Triplet
Singlet
B_{1g}
coordinate

1973 Newton[19] (ab initio SCF and GVB 4-31G)

1975 Dewar[42] (MINDO-3)

1968 Allinger[15b] (PP, doubly excited CI)

1968 Buenker-Peyerimhoff[18] (ab initio SCF, extended CI)

1977 Kollmar-Staemmler[59] (ab initio SCF, π-space CI)

1978 Borden-Davidson-Hart[60] (ab initio SCF, π-, δ-space CI)

FIGURE 21. Energy Profiles of the Lowest Singlet and Triplet States of 1 by Various Theoretical Treatments.

> "Fortunately science, like the nature to which it belongs is neither limited by time nor by space. It belongs to the world, and is of no country and no age. The more we know, the more we feel our ignorance; the more we feel our ignorance the more we feel how much remains unknown."
>
> SIR HUMPHRY DAVY (1825)

CONCLUDING REMARKS

This study has shown that the ring of cyclobutadiene is not square, but as noted above, it has not elucidated the exact geometry of the molecule. It is often difficult, if not impossible, to make reliable structural and vibrational assignments for reactive chemical species with the matrix-infrared data alone. Thus, the need for further reliable evidence prompted Andrews,[61] Claassen,[62] Nibler,[63] and Ozin[64] to study matrix-isolated species by Raman spectroscopy. Their results have unequivocally demonstrated the usefulness of the matrix-Raman experiment for obtaining data complementary to those obtained from the infrared work. Nibler[63] and Ozin[65] also showed the viability of matrix-Raman-depolarization measurements[45,47] adding a valuable new tool for matrix-isolation studies. They found that provided the matrix is transparent, depolarization of the incident laser beam and of the scattered Raman light is minimal, and experimental depolarization ratios are meaningful for matrix-isolated species. Although perfectly transparent matrices are in practice difficult to prepare and non-ideal depolarization ratios inevitably result from translucent matrices, the data already gathered have often permitted symmetry assignments. It was found that for ideal Raman scattering from matrices (with 90°

laser illumination collection), a band may be assigned to a totally symmetrical mode if its depolarization ratio is less than 3/4.[66]

At this point, further evidence to define the geometry of the cyclobutadiene ring is needed. This may be provided by the line positions and depolarization ratios in the Raman spectra of the $\underline{h}_4$ and $\underline{d}_4$ species, 1 and 28. Two strong bands due to symmetrical C-H stretching (A_g) and symmetrical C=C ring distortion (A_g) would be expected in the Raman spectrum, as well as a medium intensity band arising from the C-C ring distortion (B_{1g}). Additional useful information may be obtained through a re-investigation of the infrared spectra of the partially isotopically substituted species (Table 2, p. 36), particularly of the dideuteriocyclobutadienes. In the latter two cases, because of the change in symmetry, the so far unobserved in-plane H-C=C bending vibration of B_{1u} symmetry (point group D_{2h}) may show strongly (Table 6).

The integrated intensity of a fundamental infrared band is proportional to the components, μ_x, μ_y, and μ_z, of the dipole moment along axes fixed by convention within the molecule.[67] It has been shown that "two intensity sum rules" can be formulated over all coordinates of a given symmetry class.[68] These rules can be used to evaluate the intensities of two modes belonging

		C_4H_4	C_4D_4	C_4H_3D	C_4HD_3	$C_4H_2D_2$		
						1,2	1,4	1,3
		D_{2h}	D_{2h}	C_s	C_s	C_{2v}	C_{2v}	C_{2h}
ν_1	symmetrical C-H(D) stretching	-	-	3000	2200	2997	2991	-
ν_2	symmetrical C-D(H) stretching	-	-	2200	3000	2250	2228	-
ν_3	C=C stretching	-	-	1500	1400	1409	1422	-
ν_4	symmetrical C-H(D) bending	-	-	1100	1000	1020	1174	-
ν_5	C-C stretching	-	-	900	700	827	923	-
ν_6	in-plane C-H(D) bending	-	-	750	650	686	776	-
ν_7	out-of-plane C-H(D) bending	-	-	700	550	-	-	-
ν_8	out-of-plane C-H(D) bending	-	-	550	700	-	-	-
ν_9	ring angle deformation	-	-	300	300	299	299	-
ν_{10}	ring puckering	-	-	50	50	-	-	50
ν_{11}	out-of-plane C-H(D) bending	574	422	600	450	615	621	708
ν_{12}	out-of-plane C-H(D) bending	-	-	450	600	455	458	480
ν_{13}	C-H(D) stretching	3050	2250	3000	2200	2980	2987	2989
ν_{14}	C-H(D) stretching	2900	2200	2200	3000	2196	2219	2226
ν_{15}	C=C stretching	1540	1455	1500	1400	1511	1499	1498
ν_{16}	in-plane C-H(D) bending	1223	1054	1200	1100	1211	1127	1163
ν_{17}	in-plane C-H(D) bending	974	713	1000	700	1014	792	851
ν_{18}	asymmetrical C-C stretching	740	604	700	600	664	626	639

TABLE 6. Modes of Vibration of Rectangular Cyclobutadiene.

to the same symmetry type and that also couple. Bos,[69] Haas and Sheline,[70] and more recently Ogden[71] and Ozin[72] have found that these intensity sum rules can be used to predict relative absorption intensities of infrared-active modes of vibration. Close agreement between measured integrated absorptions and calculated intensities was reported for a variety of species. Such agreement provides further support for the correctness of the geometry assumed for the normal coordinate calculations for these species. Cyclobutadiene should be amenable to this treatment.[73]

"You can extract from alembic or jar
From the physical basis of black coal tar
Oil and ointment, wax and wine
And the lovely colors called aniline
You can make anything from a salve to a star
If you only know how, from black coal tar."

PUNCH MAGAZINE (1884)

CHAPTER V

EXPERIMENTAL

All melting points and boiling points are uncorrected. Melting points were taken on a Thomas-Hoover capillary melting point apparatus.

The ^1H nuclear magnetic resonance spectra were recorded on a Varian A-60 Analytical Spectrometer or on a Varian HA-100 Spectrometer. Tetramethylsilane was used as an internal standard unless otherwise stated. In reporting ^1H nmr spectral data, the following abbreviations are used.

s, singlet
d, doublet
t, triplet
q, quartet
m, multiplet
dd, doublet of doublets

The infrared spectra were obtained on a Perkin-Elmer 457 Grating Infrared Spectrophotometer. In reporting ir spectral absorptions, the following abbreviations are used.

s, strong
m, medium
w, weak
vs, very strong

The mass spectra were measured with A.E.I. MS-12 and MS-50 Spectrometers.

The gas-liquid-chromatographic analyses were performed on a Hewlett-Packard 7620 Research Chromatograph equipped with an electronic integrator. A flame ionization detector and 1.8 m x 0.3 cm columns were used (packing indicated in the text).

The thin-layer-chromatographic analyses were carried out on 3 x 7 cm, 0.25 mm Woelm silica gel F254 plates. For preparative purposes, square 20 x 20 cm, 0.25 mm - 2.0 mm thick, silica gel EM® HF and 366 (type 60) plates without binder were used. The plates were activated at 110°C for 16 h and stored under anhydrous conditions.

Column chromatography was performed using MN® silica gel 60, 70-270 Mesh, Activity I.

All reactions were carried out under a dry argon atmosphere unless otherwise specified in the text. A Büchi rotary evaporator connected to a water aspirator was used for the removal of solvents from all reaction mixtures.

The isotopic enrichment of all deuterated compounds was determined by mass spectroscopy unless otherwise specified in the text.

In the lithium aluminum hydride (deuteride) reductions the yields quoted are of product recovered directly from the reaction mixture.

Solvents

Acetone

Commercial reagent grade acetone from a freshly opened bottle was used.

Benzene

Commercial thiophene-free benzene was pre-dried overnight at room temperature over P_2O_5, then was heated to refluxing over freshly cut sodium and distilled (benzophenone was used as indicator). The freshly distilled solvent was stored over sodium wire.

Carbon Tetrachloride

The reagent grade solvent was purified by passing through a column of basic alumina.

Chloroform

Commercial grade chloroform was usually employed. Small quantities of chloroform were purified by passage through a column of activated alumina or silica gel.

Dichloromethane

Dichloromethane was pre-dried with either $CaCl_2$ or preferably over 4Å molecular sieves, then was heated to refluxing over P_2O_5 and distilled. It was stored over 4Å molecular sieves.

1,2-Dichloroethane

This solvent was purified by the same procedure as described for dichloromethane.

Dimethylsulfoxide

The commercial grade solvent was purified by drying over Linde 4Å molecular sieves overnight, then distilled under reduced pressure from CaH_2, bp: 75.0-77.0°C (12 Torr).

Ethanol

Preliminary drying of ethanol was achieved by heating under reflux for 6-8 h over either CaO or sodium and diethyl phthalate, then distilling.

Anhydrous ethanol was prepared by distilling the pre-dried solvent from its magnesium salt.

Ether

Mallinckrodt anhydrous ether from freshly opened cans was used without further purification, otherwise it was distilled from sodium-benzophenone ketyl under argon.

Ethyl Acetate

The crude solvent was pre-purified by treatment with anhydrous K_2CO_3, then was distilled from anhydrous $CaSO_4$.

n-Heptane

The bulk-quantity grade solvent was pre-dried over 4Å molecular sieves and then distilled from P_2O_5. The anhydrous product was stored over sodium wire.

Hexamethylphosphoric Triamide (HMPA, HMPT)

The reagent grade product was pre-dried overnight with CaH_2 and then distilled under reduced pressure from fresh CaH_2, bp: 113-114°C (10 Torr).

Hexanes (Skelly B)

See *n*-heptane.

Methanol

A small quantity of magnesium was treated with pure methanol under Ar and the mixture was added to the bulk of the wet methanol after the formation of methoxide had begun. Under these conditions, 5-10 g of magnesium turnings were required per litre of methanol. After the vigorous reaction had ceased, the mixture was heated under refluxing for 2-3 h and distilled. The distillate was always handled under argon.

n-Pentane

n-Pentane was dried by treatment with anhydrous $MgSO_4$, decanting, heating under reflux over P_2O_5 and fractionally distilling through a column packed with glass helices.

Tetrahydrofuran

The reagent grade solvent was pre-dried over 4Å molecular sieves or granular $CaCl_2$ for at least one week, then was added to a stirred (Caution !!, local overheating may cause serious explosions) suspension of excess sodium in anhydrous tetrahydrofuran (blue) containing benzophenone. If reasonably pre-dried tetrahydrofuran was used the blue color of the sodium-benzophenone ketyl persisted or re-appeared after a few minutes refluxing (occasionally, fresh benzophenone had to be added). Anhydrous tetrahydrofuran was obtained by distillation after 1-2 h.

Toluene

See benzene.

Preparation of Lithium Aluminum Hydride (Deuteride) - Tetrahydrofuran Solution

Approximately 3 mol of solid lithium aluminum hydride (Note 1) were added under argon to 1 ℓ of anhydrous tetrahydrofuran and the suspension was heated to refluxing with stirring for 48 h (Note 2). An insoluble precipitate was formed and although it appeared to be very bulky, it was easily removed by filtration (sintered glass funnel) and amounted to less than 1% of the original hydride (Note 3).

For standardization, 1 ml of solution was decomposed with an excess of 0.1 M aqueous HCl which was then back titrated with 0.1 M aqueous NaOH using as indicator 0.1% of bromophenol blue in ethanol. The equivalence point was reached when the first green shade appeared (Note 4).

Notes

1. Caution!! Lithium aluminum hydride may ignite spontaneously. For smothering a lithium aluminum hydride fire use a pail of powdered limestone ($CaCO_3$) and a long-handled shovel. In no case use water, carbon dioxide, or a chemical extinguisher.
2. The solubility of lithium aluminum hydride in tetrahydrofuran is only 13 g/100 g at 25°C and to attain

this degree of solubility it is necessary to concentrate a more dilute solution.[74]

3. Filtration should be carried out under argon and after all solids have settled down. The supernatant liquid may not be clear.

4. Lithium aluminum hydride residues were disposed off using ethyl acetate. The residue was either diluted or suspended in ether or tetrahydrofuran under argon and cooled to 0°C while with stirring ethyl acetate was added dropwise until all active hydride was destroyed.

1,4-Cyclohexadienedicarboxylic Anhydride (32)

To 10.33 g (52.6 mmol) of dimethyl dihydrophthalate (Note 1) in 50 ml of 90% formic acid was added 10 g (7 ml) of methanesulfonic acid in small portions with stirring and the resulting colorless solution was heated at reflux for six h.[76] After cooling to room temperature the reaction mixture was poured into 250 ml of a 1:1 mixture of ice-cold water and brine. An adequate amount of ether (500-600 ml) was added to obtain two distinct layers and the two phases were shaken very vigorously (Note 2). The aqueous layer was further extracted with ether (2 x 250 ml). The combined yellow ether extracts were washed with a 1:1 mixture of ice-cold water and brine (8 x 50 ml) and then with ice-cold brine (2 x 100 ml). The organic layer was dried over anhydrous Na_2SO_4 and the ether removed on a rotary evaporator to give a solid suspended in some remaining formic acid. This residue was dissolved in warm ether-toluene, and the solvents were removed in vacuum to give 8.64 g of a yellowish solid which was then suspended in 150 ml of toluene containing 5 ml of acetic anhydride. The mixture was heated at reflux overnight under argon, allowed to cool to room temperature, filtered and concentrated in vacuum to dryness to afford 7.74 g (98%) of solid, mp 129-140°C (Note 3).

Physical Data for 32

mp: 147-148° (ethyl acetate, sublimed 100°, 50 mTorr)

ir ($CDCl_3$) cm^{-1}: 3040 (w), 2820 (w), 2890 (w), 1845 (s), 1770 (vs), 1690 (w), 1640 (w), 1428 (m), 1265 (s), 1180 (w), 1060 (m)

^1H nmr, 60 MHz ($CDCl_3$) δ: 3.12 (d, J = 1 Hz, 4), 5.92 (d, J = 1 Hz, 2)

mass spectrum, m/e (relative intensity): 151 (1, $M+1^+$), 150 (10, M+), 148 (0.2, $M-2^+$)

Notes

1. This diester was prepared by the method of Alder, see reference 75.
2. The direct product of the hydrolysis contains a 30 to 40% of the corresponding diacid. The limited solubility of this compound in wet ether may reduce dramatically the yield of anhydride if the extraction is incomplete.
3. The product can also be obtained in one step by Diels-Alder reaction of 1,3-butadiene with acetylene dicarboxylic acid.[75b]

Cyclobutadiene-$\underline{d}_4$-iron Tricarbonyl (33)

To a stirred solution of 10.00 g (52 mmol) of cyclobutadiene-$\underline{h}_4$-iron tricarbonyl (Note 1) in 130 ml of chloroform (Note 2) under argon was added 40 ml of trifluoroacetic acid-$\underline{d}$ (Note 3), and the resulting mixture was stirred at 50°C in the dark for 13 h. The brownish orange solution was then allowed to cool to room temperature, poured into 200 ml of ice-cold water, and extracted with n-pentane (1 x 270 ml and 3 x 25 ml). The combined extracts were washed successively with two 50-ml portions each of distilled water, saturated aqueous $KHCO_3$ and brine, dried over anhydrous $MgSO_4$, and finally concentrated to a volume of 50 ml. The concentrate was diluted with fresh chloroform and the above process repeated two more times. The solvent after the final work-up was removed by distillation (Note 4) and the remaining brownish liquid was distilled to give 7.91 g (77%) of cyclobutadiene-$\underline{d}_4$-iron tricarbonyl as pale yellow crystals with a deuterium content of 98.3 atom % D (Note 5).

Physical Data for 33

bp: 50-55° (0.3 Torr)

ir (neat) cm^{-1}: 2060 (s), 1980 (vs), 1240 (w), 1180 (w), 730 (w), 670 (w), 630 (w)

^1H nmr, 60 MHz ($CDCl_3$) δ: The absorption at 3.93 (s) was absent.

Notes

1. Cyclobutadiene-$\underline{h}_4$-iron tricarbonyl was prepared by Pettit's procedure[77] from cyclooctatetraene[78] (Fluka, Switzerland) and diiron enneacarbonyl.[79]
2. Anhydrous, alcohol-free chloroform was used.
3. Trifluoroacetic acid-$\underline{d}$ was prepared from deuterium oxide, 99.8 atom % D, and the corresponding anhydride in the following manner.

   To 9.6 g (8.7 ml, 0.48 mol) of deuterium oxide was added 100 g (0.47 mol) of freshly distilled trifluoroacetic anhydride (Eastman Kodak) at 0-5°C under argon with stirring. The reaction mixture was allowed to warm to room temperature and distilled under argon to give 101.6 g (93%) of trifluoroacetic acid-$\underline{d}$, bp 73-74°C, 99.5 atom % D.
4. The bulk of the solvent was removed at 75°C (atmospheric pressure) and the last traces at 50°C (3 Torr).
5. This procedure has been developed on the basis of Pettit's earlier observation of deuterium exchange in cyclobutadiene-$\underline{h}_4$-iron tricarbonyl by electrophilic aromatic substitution in the presence of trifluoroacetic acid-$\underline{d}$.[80] The deuterium content was estimated by ^{1}H nmr using maleic anhydride as standard.

11,13-Bis-(oxo)-12-oxa-tetracyclo[4.4.3.0.0^{2,5}]trideca-3,8-diene-2,3,4,5-d_4 (34)

In a 500-ml, round-bottomed flask with four vertical necks, fitted with a mechanical stirrer, gas inlet, Claisen tube and gas bubbler (Note 1) was placed 2.35 g (15.7 mmol) of 1,4-cyclohexadienedicarboxylic anhydride dissolved in 50 ml of a 1:9 mixture of hexane and acetone. The flask was cooled in an ice-water bath, and while stirring vigorously, 1 ml of a solution of 3.09 g (15.7 mmol) of cyclobutadiene-d_4 iron tricarbonyl in 10 ml of a 1:9 mixture of hexane and acetone was added and then 2.6 g of finely powdered ceric ammonium nitrate[81] was dropped into the mixture in small portions. This process was repeated until all approximately 10 ml of the iron tricarbonyl solution and the 26 g (47.1 mmol) of ceric salt had been added. The total addition required 30 minutes (Note 2). The ice-cold reaction mixture was stirred for an additional 30 minutes, by which time carbon monoxide evolution had ceased, and then was poured into 320 ml of ice-cold water containing 25 g of NaCl, and extracted with ether (1 x 500 ml and 4 x 150 ml). The combined extracts were washed with a 1:1 mixture of water and brine (4 x 50 ml) and ice-cold brine (2 x 50 ml) and dried over anhydrous Na_2SO_4.

Removal of the solvent on the rotary evaporator gave 3.30 g of a mixture of starting material and adduct. A suspension of this mixture in 80 ml of anhydrous methanol was heated at reflux for 30 minutes under argon. The resulting yellow solution was cooled to 40-45°C, and then poured into 400 ml of ice-cold ether, and extracted with five 50-ml portions of an aqueous solution, 5% in $NaHCO_3$ and 10% in NaCl. The ether layer was washed with brine (2 x 50 ml) and dried over anhydrous Na_2SO_4. Removal of ether under reduced pressure gave 2.15 g of a brown solid which was sublimed (90°C, 25 mTorr) to afford 1.97 g (60%) of pure product.

Physical Data for **34**

mp: 159-160° (tetrahydrofuran-ether)

tlc: dichloromethane, 0.4; hexanes-ethyl acetate (5:2), 0.8

ir ($CHCl_3$) cm^{-1}: 3060 (w), 2990 (w), 2940 (w), 2900 (w), 2860 (w), 2340 (w), 2270 (m), 1850 (s), 1780 (vs), 1650 (w), 1610 (w), 1445 (m), 1380 (w), 1292 (m), 1275 (s), 1240 (m), 1220 (s), 1160 (w), 1100 (m), 1030 (w)

^1H nmr, 60 mHz ($CDCl_3$) δ: 3.58 (dd, J = 3 Hz and 2 Hz, 4), 6.00 (t, J = 3 Hz, 2)

mass spectrum, m/e (relative intensity): 207 (1, $M+1^+$), 206 (10, M+), 205 (0.5, $M-1^+$)

Notes

1. The reaction must be run in a well-ventilated fume hood because of the evolution of carbon monoxide and the high toxicity of the iron carbonyl complex.
2. Shorter or longer addition times consistently led to lower yields of adduct.

1,6-Bis-(hydroxymethyl)-tricyclo[4.4.0.$0^{2,5}$]deca-3,8-diene-2,3,4,5-d_4 (35)

To a stirred solution of 1.21 g (5.86 mmol) of the anhydride 34 in 150 ml of anhydrous tetrahydrofuran under argon, contained in a 500-ml, round-bottomed flask, was added dropwise 9.0 ml of 1.053 M $LiAlH_4$-tetrahydrofuran solution. The reaction was exothermic and a precipitate of aluminum complexes was formed. An efficient reflux condenser was attached to the flask and the mixture heated at reflux for 10 h. The reaction was quenched with excess water (819 mg, 45.5 mmol) in 250 ml of anhydrous tetrahydrofuran to give a colorless, thick suspension of lithium and aluminum salts. After heating at reflux for 8 h, the warm suspension was filtered through a Celite pad. The inorganic salts were washed with three 100-ml portions of tetrahydrofuran and the combined filtrates were concentrated to dryness on the rotary evaporator to afford 1.00 g (87%) of a colorless solid.

The inorganic salts and Celite were transferred to the reaction flask, 300 ml of tetrahydrofuran was added and the mixture refluxed with stirring for 10 h. Filtration and solvent removal gave 100 mg (8.7%) of solid. Repetition of this extraction afforded an additional 46 mg (4%) of diol. The total amount of diol recovered was 1.14 g (99%).

The product was dried by azeotropic removal of water (anhydrous tetrahydrofuran-toluene) on the rotary evaporator, and in high vacuum (25 mTorr) over P_2O_5 and used in the next step.

Physical Data for **35**

mp: 134-136°

ir ($CHCl_3$) cm^{-1}: 3620 (s), 3340 (vs), 3040 (m), 2985 (w), 2910 (s), 2870 (s), 2840 (m), 2280 (w), 2220 (m), 1640 (w), 1430 (s), 1260 (m), 1200 (w), 1120 (m), 1040 (m), 1010 (s)

^1H nmr, 60 MHz ($CDCl_3$) δ: 1.88 (m, 2), 2.68 (d, J = 14 Hz, 2), 3.34 (s, 2), 3.48 and 3.98 (AB q, J = 11 Hz, 4), 5.97 (dd, J = 4 and 3 Hz, 2)

mass spectrum, m/e: 178 ($M-18^+$ $C_{12}H_{10}D_4O$)

12-Oxa-tetracyclo[4.4.3.0.$0^{2,5}$]trideca-3,8-diene-2,3,4,5-d_4 (36)

An oven-dried, 300-ml, 3-necked, round-bottomed flask was fitted with an egg-shaped magnetic stirring bar, two septa and a precision-dropping funnel (Note 1). The system was cooled to room temperature under a stream of argon and a static argon atmosphere was maintained throughout the experiment. Using syringes, 1.098 g (1.3 ml, 7.7 mmol, 1.2 equiv) of 2,2,6,6-tetramethylpiperidine and 25 ml of anhydrous tetrahydrofuran were added to the flask in that order. The solution was cooled to between -20 and -25°C with a dry ice-acetone bath and 4.6 ml (7.08 mmol, 1.05 equiv) of n-butyllithium in hexane was added dropwise with stirring. The yellowish solution was allowed to warm up to room temperature, and then cooled to -80°C. A solution of 637 mg (3.24 mmol, 1.0 equiv) of diol 35 in 10 ml of anhydrous tetrahydrofuran and 30 ml of anhydrous hexamethylphosphoric triamide were added with stirring in a continuous stream. The flask which had contained the diol and the syringe were rinsed with two 10-ml portions of tetrahydrofuran which were added to the reaction flask. When the addition was complete and the reaction mixture had cooled sufficiently, a colorless solid formed and stirring became impossible. The dry ice-acetone bath was removed, the frozen hexamethylphosphoric triamide melted and stirring could be resumed. The mixture was allowed to warm to room temperature to give a light colored homogeneous solution. While stirring vigorously, a solution of 927 mg (4.86 mmol, 0.7 equiv) of p-toluenesulfonyl chloride (Note 2) in 100 ml of anhydrous tetrahydrofuran was added dropwise over a period of 8 h (Note 3). The light yellow reaction mixture that resulted was poured into 280 ml of ice-cold 3% aqueous hydrochloric acid containing 28 g of NaCl, and extracted with ether (1 x 200 ml, and 4 x 100 ml). The combined ether extracts were washed with ice-cold 5% aqueous hydrochloric acid (6 x 50 ml), ice-cold brine (6 x 50 ml), saturated aqueous $KHCO_3$ (50 ml) and finally with brine (2 x 50 ml). The organic layer was dried over anhydrous Na_2SO_4. Solvent removal on the rotary evaporator (Note 4) gave 3 g of oil. A solution of the oil in 50 ml of anhydrous dichloromethane was further dried over anhydrous Na_2SO_4, filtered through a Celite pad, and the solvent removed in vacuum (Note 4) to afford 890 mg of a clear homogeneous oil which showed two spots on tlc (Note 5).

The tetracyclic compound was chromatographed on 50 g of silica gel in a 3-cm diameter column (Note 6). From the first 70 ml of eluent was recovered 198 mg of a colorless oil which crystallized in vacuum and was identified as p-toluenesulfonyl chloride. Fractions 22 to 70 were combined and concentrated in vacuum (Note 4) to give 566 mg (98%) of yellow oil. Distillation (80-100°C, 20 Torr) afforded 520 mg (90%) of pure ether **36**, 98 ± 1 atom % D.

Physical Data for **36**

bp: 90° (10 Torr)

ir ($CHCl_3$) cm^{-1}: 3040 (s), 2918 (vs), 2840 (vs), 2310 (w), 2220 (s), 1635 (w), 1435 (s), 1365 (w), 1260 (w), 1210 (m), 1135 (w), 1115 (w), 1070 (s), 1035 (s), 970 (w)

^1H nmr, 60 MHz ($CDCl_3$) δ: 2.18 (d, J = 3 Hz, 4), 3.40 and 3.64 (AB q, J = 9 Hz, 4), 6.00 (t, J = 3 Hz, 2)

mass spectrum (m/e): Calcd for $C_{12}H_{10}D_4O$ m/e: 178.1296

Found m/e: 178.1285

Notes

1. The funnel and magnetic bar were dried overnight in the oven at 120°C.
2. Acid free p-toluenesulfonyl chloride was used in these preparations.[82]

   Baker quality tosyl chloride, 10.0 g, was dissolved in 50 ml of boiling anhydrous dichloromethane, the solution allowed to cool and 250 ml of anhydrous n-pentane added to precipitate impurities. The resulting cloudy suspension was briefly cooled to 0°C and filtered through a Celite pad. The colorless filtrate was evaporated to dryness on the rotary evaporator to give 9.0 g of colorless-hard solid. The compound obtained in this fashion, although thought to be of analytical purity was subjected to sublimation (69-70°, 25 mTorr) to afford in 3 h 8.7 g of beautiful crystals.

3. An addition rate of 7-8 drops/minute was closely maintained.
4. The temperature of the water bath was kept at 20-25°C during evaporation of the bulk of the solvent. The last traces were removed at 10-15°C and 100 Torr.
5. 1% Methanol-dichloromethane: 0.5, product; 0.9, tosyl chloride.
6. Dichloromethane was used as eluent, 10-ml fractions were collected with the aid of a fraction collector. Tosyl chloride was detected by tlc-uv. The remaining, tosyl chloride free fractions were then examined by glc (10 µl): UC-W98, injection port, 200°C; oven program, 150°C for 1 min, heated at 15°C/min to 200°C, 200°C for 1 min.

4,13-Bis-(oxa)-pentacyclo[5.4.3.0.0^{2,6}.0^{3,5}]tetradeca-9-ene-2,3,5,6-d_4 (**37**)

A solution of 520 mg (2.91 mmol) of the diene **36** in 15 ml of anhydrous dichloromethane was placed in a 100-ml, round-bottomed flask, then 710 mg (1.2 equiv) of 85% m-chloroperbenzoic acid in 35 ml of dichloromethane was added dropwise with stirring over a period of 10 min. The reaction mixture was stirred for 1 h, diluted with 150 ml of dichloromethane and extracted with three 50-ml portions of an aqueous solution 5% in Na_2SO_3 and 5% in $KHCO_3$. The organic layer was washed twice with 50-ml portions of aqueous 5% $KHCO_3$ and twice with 25-ml portions of brine. The resulting colorless solution was dried over anhydrous Na_2SO_4 and the solvent removed in vacuum to give 580 mg of colorless oil. The epoxide was purified by column chromatography (Note 1) to yield 551 mg (95%) of product, 98 ± 1 atom % D (Note 2).

Physical Data for **37**

bp: 80-85° (0.3 Torr)

^{1}H nmr, 60 MHz ($CDCl_3$) δ: 2.15 (d, J = 3 Hz, 4), 3.30 (d, J = 10 Hz, 2), 4.26 (d, J = 10 Hz, 2), 5.98 (t, J = 3 Hz, 2)

mass spectrum (m/e): Calcd for $C_{12}H_{10}D_4O_2$ m/e: 194.1245
Found m/e: 194.1237

Notes

1. The crude epoxide was adsorbed on 20 g of silica gel in a 2.5-cm column. Unreacted diene was eluted with dichloromethane and then the epoxide was eluted with 2% methanol-dichloromethane. Fractions of

10 ml were collected and the progress of the chromatography was followed by glc (10 µl): UC-W98; injection port, 200°C; oven program, 150°C for 1 min; temperature raised to 250°C at 15°C per min then holding at 250°C for 2 min.

2. This product was diene free but contained small amounts of a mixture of diepoxides which did not affect at all the result of the overall sequence.

4,13-Bis-(oxa)-pentacyclo[5.4.3.0.0^{2,6}.0^{3,5}]tetradeca-8,10-diene-2,3,5,6-d_4 (**39**)

To a stirred solution of 493 mg (2.53 mmol) of epoxide **37** in 25 ml of absolute dichloromethane was added 10 µl of absolute ethanol. The mixture was cooled under argon to -10 to -20°C with a dry ice-acetone bath and 27 ml (2.7 mmol) of freshly prepared bromine-dichloromethane solution (Note 1) added dropwise until the bromine color did not fade. The resulting reaction mixture was allowed to warm to room temperature and further stirred for 5 min, then diluted with 150 ml of dichloromethane and washed with three 50-ml portions of aqueous 5% $KHCO_3$, 50 ml of brine and dried over anhydrous Na_2SO_4. The solvent was removed in vacuum to give 861 mg (96%) of a colorless oil. The solid dibromide **38** was obtained by thorough removal of dichloromethane by codistillation of a solution of the product in dichloromethane with n-heptane (Note 2). It was dried by azeotropic removal of water with benzene and used in the next step.

The crude dibromide was dissolved in 20 ml of anhydrous dimethyl sulfoxide. While stirring the solution under argon, 846 mg (7.53 mmol, 3.1 equiv) of freshly sublimed potassium tert-butoxide (Note 3) was added in small portions. The warm reaction mixture developed a brown color within 5 min, and after 1 h stirring at room temperature, was poured into 100 ml of ice-water and extracted with n-pentane (1 x 200 ml and 4 x 100 ml). The combined organic extracts were washed with 100 ml of distilled water, 100 ml of a 1:1 mixture of water and brine and 50 ml of brine. The yellow solution was dried over anhydrous Na_2SO_4 and concentrated to dryness on the rotary evaporator to give 200 mg (41%) of a yellow solid which was sublimed at 90-100°C (10 Torr) to afford 180 mg (37%) of colorless solid, 98 ± 1 atom % D.

Physical Data for 39

mp: 86-88° (n-pentane)

^{1}H nmr, 90 MHz ($CDCl_3$) δ: 3.28 (d, J = 5 Hz, 2), 4.32 (d, J = 5 Hz, 2), 5.73 (m, 4)

mass spectrum: no parent peak

Notes

1. Bromine (15.98 g) was dissolved in absolute dichloromethane in a 100-ml volumetric flask to give a 0.1 M solution of reagent.
2. The crude product was examined by ^{1}H nmr and the spectrum showed the complete disappearance of the triplet signal at 5.98 δ.
3. Potassium *tert*-butoxide was sublimed at 140-145°C (50 mTorr).[83]

12-Oxa-tetracyclo[4.4.3.0.0^{2,5}]trideca-3,7,9-triene-2,3,4,5-*d*$_4$ (**31a**)

A dry, 50-ml, three-necked, round-bottomed flask equipped with a thermometer, a mechanical stirrer and a rubber septum was flushed with argon and maintained under a static argon atmosphere (Note 1). The flask was charged with 15 ml of anhydrous tetrahydrofuran and cooled to -60 to -65°C in a dry ice-acetone bath. Tungsten hexachloride[84] (952 mg, 2.40 mmol) was then introduced all at once (Note 2) followed by the dropwise addition with stirring of 3.1 ml (4.77 mmol) of *n*-butyllithium in hexane while keeping the temperature of the reaction mixture below -15°C. The resulting mixture was allowed to warm gradually to room temperature. The green-brown viscous suspension became a dark-brown homogeneous solution which eventually turned green at room temperature. A solution of 230 mg (1.20 mmol) of the epoxide **39** in 7 ml of anhydrous tetrahydrofuran was added rapidly. The reaction mixture was stirred for 3 h, then poured into 50 ml of an aqueous solution, 2M in NaOH and 1.5M in sodium potassium tartrate. The resulting brownish suspension was extracted with n-pentane (1 x 100 ml and 3 x 50 ml), the combined organic extracts were washed with 5% aqueous $KHCO_3$ (5 x 20 ml), brine (2 x 20 ml) and dried over anhydrous Na_2SO_4. The n-pentane solution was filtered and analyzed by glc (Note 3) and tlc (Note 4) and found to be a mixture of three components, the major one (90%) being the desired product.

The solvent was removed in vacuum (50 Torr) to give 340 mg of clear yellow oil which was initially purified by tlc (Note 5). Bulb-to-bulb distillation (60°C, 1 Torr) provided 90 mg (42%) of a pure colorless solid, 98 ± 1 atom % D.

Physical Data for **31a**

mp: 33-35°

ir (neat) cm^{-1}: 3020 (w), 2950 (w), 2910 (w), 2840 (m), 2210 (w), 1460 (w), 1245 (w), 1210 (w), 1160 (w), 1075 (m), 1035 (m), 970 (w), 920 (m), 890 (w), 880 (w), 835 (w), 760 (m), 730 (w), 700 (vs), 620 (w), 600 (m), 495 (w), 420 (m), 360 (w)

^{1}H nmr, 60 MHz ($CDCl_3$) δ: 3.49 and 4.09 (AB q, J = 10 Hz, 4), 5.80 (m, 4)

mass spectrum (m/e): Calcd for $C_{12}H_8D_4O$ m/e: 176.1139

Found m/e: 176.1135

Notes

1. Dry argon was admitted into the flask by a hypodermic needle through the rubber septum. A static argon atmosphere was maintained throughout the subsequent reactions.
2. Dark blue crystals obtained by sublimation (60°C, 25 mTorr) of the commercial product (Alfa-Ventron) in vacuum were collected prior to reaction. A more volatile yellow impurity condensed at the top of the condenser. The yellow-blue crystals condensing in the first few hours of sublimation were usually discarded. The final sublimate composed of only dark blue crystals was collected in a dry glove-box, weighed in a dry flask under argon and quickly transferred all at once to the reaction flask.
3. For the glc (10 µl): UC-W98; injection port, 200°C; oven temperature program, 130°C for 10 min; temperature raised at 15°C per min to 250°C; temperature maintained at 250°C for 10 min.
4. Tlc: silica gel, dichloromethane, 0.2, 0.4, 0.6.

5. The oil was taken up in 2 ml of dichloromethane, spotted on two 20 x 20 cm square, 0.25 mm thick tlc silica gel plates and developed with 1% methanol dichloromethane. The second uv active band from the solvent front, which was about 2 cm wide, was scraped off, placed in a column and eluted with 100 ml of 2% methanol-dichloromethane to give a bright yellow solution. Solvent removal on a rotary evaporator (10 to 20 Torr) afforded 105 mg of a chromatographically pure yellow oil which showed two peaks on glc (Note 3).

Dimethyl 1,4-Cyclohexadienedicarboxylate-3,3,4,5,6,6-$\underline{d}_6$ (**54**)

The diester **54** was prepared according to the known procedure for the per-protio analogue.[75a] Diels-Alder reaction of 1,3-butadiene-$\underline{d}_6$ (Note 1) and dimethyl acetylenedicarboxylate afforded an excellent yield of the adduct (**54**), 98 ± 1 atom % D.

Physical Data for **54**

bp: 138-140° (10 Torr)

ir (neat) cm^{-1}: 3000 (w), 2960 (m), 2900 (w), 2840 (w), 2270 (w), 2240 (w), 2170 (w), 2080 (w), 1725 (vs), 1665 (m), 1630 (m), 1430 (s), 1330 (s), 1270 (s), 1240 (s), 1210 (s), 1065 (s), 1025 (s), 940 (w), 920 (w), 815 (m), 790 (w), 780 (w), 725 (m), 650 (m)

^1H nmr, 60 MHz ($CDCl_3$) δ: 3.70 (s, 6) (standard: *p*-di-*tert*-butylbenzene, aromatic 1H)

mass spectrum (m/e): 202 (M^+ $C_{10}H_6D_6O_4$)

Notes

1. 1,3-Butadiene-$\underline{d}_6$ was prepared by reductive dechlorination of hexachloro-1,3-butadiene. The method of Craig and Fowler[85] was followed.

1,4-Cyclohexadienedicarboxylic Anhydride-3,3,4,5,6,6-$\underline{d}_6$ (55)

This compound was prepared in the same manner as the per-protio analogue 32. A solution of 10.11 g (50 mmol) of diester 54 in 50 ml of 90% formic acid was treated with 7 ml of methanesulfonic acid under refluxing conditions. Work-up of the reaction mixture followed by treatment with acetic anhydride provided 7.70 g (99%) of product 55, 98 ± 1 atom % D. It was also obtained by direct Diels-Alder reaction of 1,3-butadiene-$\underline{d}_6$[85] and acetylenedicarboxylic acid in dioxane at 100°C.[75b]

Physical Data for 55

mp: 147-148° (ethyl acetate)

ir ($CHCl_3$) cm^{-1}: 2275 (w), 2160 (w), 2060 (w), 1850 (s), 1770 (vs), 1685 (w), 1610 (w), 1380 (w), 1285 (s), 1190 (s), 1085 (w), 1060 (w), 1030 (w), 990 (m), 890 (s), 810 (m)

^1H nmr, 60 MHz ($CDCl_3$-DMSO-$\underline{d}_6$): negative (standard: p-di-tert-butylbenzene, aromatic 2H)

mass spectrum (m/e): 157 (7, $M+1^+$), 156 (100.0, M^+ $C_8D_6O_4$), 155 (10, $M-1^+$ $C_8HD_5O_4$)

Calcd for $C_8D_6O_3$ m/e: 156.0693

Found m/e: 156.0692

11,13-Bis-(oxo)-12-oxa-tetracyclo[4.4.3.0.0^{2,5}]trideca-3,8-diene-7,7,8,9,10,10-d_6 (**56**)

The pure compound **56** was prepared and isolated in a manner similar to that described for the 2,3,4,5-d_4 analogue **34**. From 6.53 g (41.8 mmol) of anhydride **55**, 5.35 g (27.8 mmol) of cyclobutadiene-h_4-iron tricarbonyl and 46 g (83.4 mmol) of ceric ammonium nitrate in 170 ml of 10% hexane-acetone was obtained 3.9 g (70%) of yellowish solid. Sublimation (90°C, 25 mTorr) afforded 3.60 g (66%) of adduct **56** as colorless crystals, 98 ± 1 atom % D.

Physical Data for **56**

mp: 159-160° (tetrahydrofuran-ether)

ir ($CDCl_3$) cm^{-1}: 1848 (s), 1785 (vs)

^1H nmr, 60 MHz ($CDCl_3$) δ: 3.31 (t, J = 1 Hz, 2), 6.34 (t, J = 1 Hz, 2)

mass spectrum (m/e): 208 ($M^{+\cdot}$ $C_{12}H_4D_6O_3$)

1,6-Bis-(hydroxymethyl-d_2)-tricyclo[4.4.0.0^{2,5}]deca-3,8-diene-7,7,8,9,10,10-d_6 (**57**)

The diol **57** was prepared by following the procedure described for the 2,3,4,5-d_4 analogue **35**. From 3.42 g (16.4 mmol) of anhydride **56** and 40 ml (24.6 mmol, 1.5 equiv) of lithium aluminum deuteride-tetrahydrofuran solution in 200 ml of tetrahydrofuran, was obtained, after quenching with 2.5 ml of water in 500 ml of tetrahydrofuran, 3.22 g (97%) of **57** as colorless solid, 98 ± 1 atom % D.

Physical Data for **57**

mp: 135-136°

ir ($CHCl_3$) cm^{-1}: 3620 (s), 3340 (vs)

^1H nmr, 60 MHz ($CDCl_3$) δ: 2.80 (d, J = 1 Hz, 2), 6.28 (d, J = 1 Hz, 2)

mass spectrum (m/e): 184 ($M-18^+$ $C_{12}H_4D_{10}O$)

12-Oxa-tetracyclo[4.4.3.0.0^{2,5}]trideca-3.8-diene-7,7,8,9,10,10,11,11,13,13-$\underline{d}_{10}$ (**58**)

The cyclization procedure developed for the isolation of the 2,3,4,5-$\underline{d}_4$ analogue **36** was followed. The dialkoxide was prepared from 3.21 g (15.8 mmol, 1.0 equiv) of diol **57**, 5.35 g (6.4 ml, 37.9 mmol, 1.2 equiv) of 2,2,6,6-tetramethylpiperidine and 22.6 ml (34.7 mmol, 1.1 equiv) of a hexane solution of n-butyllithium using 250 ml of tetrahydrofuran and 140 ml of hexamethylphosphoric triamide as solvent. While stirring under argon, 3.76 g (19.7 mmol, 0.62 equiv) of p-toluenesulfonyl chloride in 200 ml of tetrahydrofuran was added dropwise to the dialkoxide solution over a period of 18 h. Aqueous work-up and chromatography on silica gel of the reaction mixture provided 2.81 g (96%) of colorless oil, 98 ± 1 atom % D.

Physical Data for 58

bp: 90° (10 Torr)

ir ($CHCl_3$) cm^{-1}: showed the complete disappearance of the bands at 3620 and 3340 due to the starting diol

^1H nmr, 60 mHz ($CDCl_3$) δ: 2.83 (d, J = 1 Hz, 2), 6.26 (d, J = 1 Hz, 2)

mass spectrum (m/e): 184 (M^+ $C_{12}H_4D_{10}O$)

4,13-Bis-(oxa)-pentacyclo$[5.4.3.0.0^{2,6}.0^{3,5}]$tetradeca-8,10-diene-8,9,10,11,12,12,14,14-$\underline{d}_8$ (61)

The diene 58 was subjected to a similar epoxidation-bromination-dehydrobromination sequence as was used for the 2,3,5,6-$\underline{d}_4$ compound (36). Thus, from 2.81 g (15.2 mmol) of diene 58 was obtained 1.35 g (45%) of epoxide 61 as a yellow solid, 98 ± 1 atom % D.

Physical Data for 61

mp: 87-88° (n-pentane)

^1H nmr, 60 MHz ($CDCl_3$) δ: 2.73 (d, J = 3 Hz, 2), 3.98 (d, J = 3 Hz, 2)

mass spectrum: no parent peak

12-Oxa-tetracyclo[4.4.3.0.0^{2,5}]trideca-3,7,9-triene-7,8,9,10,11,11,13,13-$\underline{d}_8$ (23d)

The epoxide 61 was deoxygenated with Sharpless' reagent (WCl_6-2$\underline{n}$-BuLi) in the same manner as described for the 2,3,4,5-$\underline{d}_4$ analogue 39. Starting with 730 mg (3.72 mmol) of freshly sublimed 61 was obtained after aqueous work-up and purification, 300 mg (45%) of colorless solid, 98 ± 1 atom % D.

Physical Data for 23d

mp: 34-35°

ir (neat) cm^{-1}: 3090 (w), 3030 (w), 2950 (w), 2260 (w), 2200 (w), 2070, 1300 (m), 1150 (m), 1050 (m), 1035 (m), 985 (w), 960 (w), 900 (m), 870 (w), 820 (m), 805 (m), 790 (s), 720 (s), 675 (vs), 575 (vs), 340 (m)

^{1}H nmr, 60 MHz ($CDCl_3$) δ: 3.20 (d, J = 1 Hz, 2), 6.30 (d, J = 1 Hz, 2)

mass spectrum (m/e): Calcd for $C_{12}H_4D_8O$ m/e: 180.1390

Found m/e: 180.1394

Phthalan (24a)

To a stirred solution of 233 mg (278 µl, 1.65 mmol) of 2,2,6,6-tetramethylpiperidine in 20 ml of anhydrous tetrahydrofuran in a 250-ml three-necked round-bottomed flask (Note 1) was added 1.0 ml (1.54 mmol) of n-butyllithium in hexane while keeping the temperature between -10 and -20°C. The resulting clear yellow mixture was allowed to warm to room temperature, stirred for 20 min and then recooled to -80°C. A solution of 95 mg (0.68 mmol) of diol 41a (Note 2) in 10 ml of tetrahydrofuran and 10 ml of hexamethylphosphoric triamide was added all at once with stirring. The triamide precipitated and stirring ceased. The reaction mixture was warmed to approximately -40°C, the solid melted and stirring was resumed. On warming to room temperature, a clear solution was formed and 2.59 mg (1.36 mmol) of p-toluenesulfonyl chloride in 30 ml of anhydrous tetrahydrofuran was added dropwise with vigorous stirring over a period of 2 h. The golden reaction mixture was poured into 300 ml of water and extracted with ether (1 x 100 ml, 2 x 50 ml). The combined ethereal extracts were washed successively with two 50-ml portions of 5% aqueous NaOH, of 5% HCl, of brine, of saturated $KHCO_3$, and finally of brine, The colorless ethereal solution was dried over anhydrous Na_2SO_4, concentrated in vacuum to 1 ml and purified by tlc (Note 3) to afford 80 mg (98%) of colorless oil (Note 4).

Physical Data for 24a

bp: 90° (20 Torr)

ir (neat) cm^{-1}: 3080 (w), 3030 (w), 2940 (w), 2850 (m), 1465 (m), 1370 (m), 1330 (w), 1265 (w), 1040 (vs), 900 (s), 740 (vs), 690 (w)

^1H nmr, 100 MHz ($CDCl_3$) δ: 5.09 (s, 4), 7.24 (s, 4)

mass spectrum, m/e (relative intensity): 121 (1, $M+1^+$), 120 (10, M^+), 119 (0.5, $M-1^+$)

Notes

1. All glassware and the magnetic stirring bar were dried overnight in the oven at 110-120°C.
2. Phthalyl alcohol was prepared by lithium aluminum hydride reduction of freshly sublimed phthalic anhydride.[86]
3. The concentrated solution was spotted on a 20 x 20 cm, 0.25 mm thick silica gel tlc plate and developed with dichloromethane. The band with Rf ~ 0.5 was scraped off, placed in a column and eluted with 100 ml of 2% methanol-dichloromethane.
4. The original preparation of phthalan involves dehydration of phthalyl alcohol over alumina at 300°C.[87]

Phthalic Anhydride-d$_4$ (40b)

A 250-ml, three-necked, round-bottomed flask was fitted with a reflux condenser and a magnetic stirring bar (Note 1) and charged with 5.0 g (92.5 mmol) of sodium methoxide (Note 2) and 40 ml of deuterium oxide (99.8 atom % D). To the resulting hot solution was added 1.00 g (3.5 mmol) of tetrachlorophthalic anhydride (Note 3) while stirring vigorously to effect solution, then 5.5 g of Ni/Al alloy in small portions were added over 30 min (Note 4). The stirred reaction mixture was heated in an oil bath at 75-80°C for 3 h (Note 5) and filtered while hot through a sintered glass funnel (10-20 μ). The metallic residue was washed with three 30-ml portions of hot water and the clear colorless filtrate was allowed to cool to room temperature before being acidified with 25 ml of 10 M hydrochloric acid at 5°C (Note 6). The cold aqueous solution was transferred to a 250-ml separatory funnel and extracted with ether (6 x 50 ml). The combined extracts were dried overnight (Na_2SO_4) to give, after solvent removal on the rotary evaporator, 596 mg (100%) of colorless phthalic acid-d$_4$. The crude material was dissolved in 50 ml of warm anhydrous tetrahydrofuran, filtered and the solution concentrated to dryness. The residue was recrystallized from 10 ml of water to afford 476 mg (80%) of hard crystals, mp 180-185°C (dec). This pure acid was refluxed in 50 ml of anhydrous benzene containing 612 mg (6 mmol) of acetic anhydride until the last traces of solid dissolved, then the volatile components were removed in vacuum at room temperature. The residual acetic acid or anhydride was codistilled with toluene to give 425 mg (80%) of **40b** as colorless solid,[88] 97.8 ± 0.2 atom % D.

Physical Data for **40b**

mp: 128-130° (benzene-cyclohexane)

ir ($CHCl_3$) cm^{-1}: 1865 (m), 1845 (s), 1785 (vs), 1390 (w), 1370 (w), 1330 (w), 1250 (m), 1220 (s), 1155 (w), 1065 (w), 940 (w), 900 (vs), 860 (w), 570 (m)

^1H nmr, 100 MHz ($CDCl_3$-DMSO-d_6): negative (standard: 1,2-dichloroethane 2H)

mass spectrum (m/e): 152 (M^+ $C_8D_4O_3$), 108 (C_7D_4O), 80 (C_6D_4), 52 (C_4D_2)

Notes

1. All glassware and the magnetic stirring bar were dried in the oven at 120°C for 48 h, then allowed to cool to room temperature under a positive pressure of argon.
2. Sodium methoxide was prepared from sodium and anhydrous methanol. The bulk of the excess methanol was distilled at atmospheric pressure and the last traces were removed at room temperature in vacuum.

The solid was collected by cracking the flask inside a glove-box under argon in the presence of P_2O_5 and was then reduced to a fine powder using an oven dried mortar cooled under argon. The resulting solid was dried for 32 h in a drying pistol (refluxing toluene) over P_2O_5 (50 mTorr).

3. Commercial tetrachlorophthalic anhydride (15.0 g) containing some free acid was recrystallized from 275 ml of anhydrous 1,2-dichloroethane and 12 ml of acetic anhydride to give 13.7 g (91%) of colorless prisms, mp 254.5-255.0°C.
4. Vigorous refluxing of the reaction mixture took place on each addition and care should be taken to prevent the foaming suspension from overflowing. An induction period was observed at first and it is best to warm up the reaction mixture before any more Ni-Al alloy is added.
5. Higher temperatures gave mainly completely saturated product while at a lower temperature some partially reduced chloride was recovered.
6. The acid was cautiously added with stirring in 1-ml portions. The aluminum oxide that formed upon neutralization dissolved in acidic medium and then 3 ml of the concentrated acid was added. Cooling was necessary due to disproportionation of $AlCl_3$ into Al_2O_3 and HCl in the hot reaction mixture.

Phthalyl Alcohol-3,4,5,6-$\underline{d}_4$ (41b)

A solution of 100 mg (0.65 mmol) of phthalic anhydride-$\underline{d}_4$ in 10 ml of anhydrous tetrahydrofuran was placed in a 100-ml, round-bottomed flask and with stirring, 0.7-0.8 ml of 1.05 M lithium aluminum hydride-tetrahydrofuran solution was added dropwise. The resulting colorless suspension was stirred at room temperature for 5 h to give a transparent colorless solution which was quenched with an excess of water (67 μl). The thick suspension was stirred at room temperature for 3 h, filtered through a Celite pad and the solid rinsed with two 5-ml portions of tetrahydrofuran. The combined filtrates were concentrated to dryness in vacuum to afford 75 mg (81%) of colorless solid. The inorganic salts were transferred back to the reaction flask, suspended in 20 ml of tetrahydrofuran, and stirred at room temperature for 3 h. The suspension was filtered as above and this sequence repeated once more. Solvent removal from the combined filtrates gave 14 mg (15%) of solid. The crude material was purified by tlc (Note 1) affording 83 mg (90%) of colorless crystals, 97.8 ± 0.2 atom % D (Note 2).

Physical Data for 41b

mp: 62-64°

ir ($CHCl_3$) cm^{-1}: 3620 (s), 3340 (vs)

^{1}H nmr, 60 MHz ($CDCl_3$) δ: 4.40 (s, 2), 4.64 (s, 4)

mass spectrum (m/e): 124 (100.0, M-18$^+$ $C_8H_4D_4O$), 123 (77.7, $C_8H_3D_4O$), 122 (11.0, $C_8H_4D_3O$), 95 (70.0, $C_7H_3D_4$), 94 (24.3, $C_7H_4D_3$)

Notes

1. The diol was dissolved in 2 ml of dichloromethane and spotted on two 20 x 20 cm, 0.25 mm thick tlc silica gel plates, which were developed with 2% methanol in 1:1 hexane-ethyl acetate. The slowest moving uv active band was scraped off, placed in a column and eluted with 100 ml of 5% methanol-ethyl acetate. Solvent removal in vacuum gave the pure product.
2. This material was dried by azeotropic removal of water with chloroform-benzene. The resulting solid was ground to a powder and further dried at room temperature in vacuum over P_2O_5.

1,3-Dihydroisobenzofuran-3,4,5,6-$\underline{d}_4$ (Phthalan **24b**)

This compound was prepared in the same manner as the per-protio analogue **24a**. From 83 mg (0.58 mmol) of the corresponding diol **41b** was obtained 60 mg (83%) of a colorless oil, 97.8 ± 0.2 atom % D.

Physical Data for **24b**

bp: 80-100° (10 Torr)

ir (neat) cm^{-1}: 2950 (w), 2850 (s), 2270 (w), 1590 (w), 1475 (w), 1360 (s), 1295 (m), 1165 (w), 1135 (m), 1060 (vs), 1000 (s), 900 (s), 860 (m), 830 (w), 785 (w), 665 (w)

^1H nmr, 60 MHz ($CDCl_3$) δ: 5.12 (s, 4), the signal at 7.25 was undetectable (standard: 1,2-dichloroethane, 2H)

mass spectrum (m/e): 124 (40, M^+ $C_8H_4D_4O$), 123 (30, $C_8H_3D_4O$), 122 (7, $C_8H_4D_3O$), 95 (100, $C_7H_3D_4$), 94 (40, $C_7H_4D_3$)

Phthalyl Alcohol-1',1',2',2'-$\underline{d}_4$ (**41c**)

An oven-dried, 100-ml, round-bottomed flask was charged under argon with 140 mg (3.3 mmol) of solid lithium aluminum deuteride (99 atom % D) which was suspended in 30 ml of anhydrous tetrahydrofuran. A solution of 444 mg (3.0 mmol) of phthalic anhydride in 10 ml of tetrahydrofuran was then added. A very thick precipitate formed and the mixture was stirred while heating under reflux for 7 h. The resulting yellowish suspension was quenched with an excess of water (260 µl) and refluxed overnight with stirring. The warm tetrahydrofuran suspension was filtered through a Celite pad and the solvent removed in vacuum to give 388 mg (90%) of yellowish crystals. The inorganic salts were transferred back to the reaction flask, suspended in 50 ml of tetrahydrofuran, heated to refluxing for 3 h, then filtered as described above and this sequence repeated once more. Solvent removal from the combined filtrates gave 21 mg (6%) of colorless solid. The combined crude material was purified by tlc (Note 1) affording 388 mg (90%) of colorless crystals, 99 ± 1 atom % D (Note 2).

Physical Data for **41c**

mp: 62-64°

ir ($CHCl_3$) cm^{-1}: 3630 (s), 3320 (vs)

^1H nmr, 60 MHz ($CDCl_3$-DMSO-d_6) δ: 4.80 (s, 2), 7.30 (m, 4)

mass spectrum (m/e): 124, ($M-18^+$ $C_8H_4D_4O$)

Notes

1. The diol was dissolved in 4 ml of 1% methanol-dichloromethane and spotted on three 20 x 20 cm, 1.0 mm thick tlc silica gel plates, which were developed with 2% methanol in 1:1 hexane-ethyl acetate. The fastest moving uv active band was scraped off, placed in a column and eluted with 150 ml of 10% methanol-ethyl acetate to give upon solvent removal, the pure product.
2. This material was dried by azeotropic removal of

water with anhydrous benzene. The resulting solid mass was reduced to a fine powder and further dried at room temperature in vacuum over P_2O_5.

1,3-Dihydroisobenzofuran-2,2,7,7-d_4 (Phthalan **24c**)

The pure compound **24c** was prepared and isolated in a manner similar to that described for the per-protio phthalan (**24a**). From 142 mg (1.0 mmol) of phthalyl alcohol-1',1',2',2'-d_4 (**41c**) was obtained 90 mg (87%) of yellowish oil, 99 ± 1 atom % D.

Physical Data for **24c**

bp: 80-100° (10 Torr)

ir (neat) cm^{-1}: 3080 (w), 3050 (w), 3030 (w), 2180 (m), 2120 (m), 2060 (m), 1480 (m), 1460 (s), 1330 (w), 1310 (w), 1255 (w), 1240 (w), 1195 (w), 1100 (s), 1080 (w), 1035 (vs), 1020 (w), 1000 (w), 940 (w), 830 (m), 725 (vs), 680 (w)

^1H nmr, 100 MHz ($CDCl_3$) δ: the signal at 5.12 was undetectable, 7.25 (s, 4) (standard: 1,2-dichloroethane, 2H)

mass spectrum (m/e): 124 (100, M^+ $C_8H_4D_4O$), 123 (10, $C_8H_3D_4O$), 122 (50, $C_8H_4D_3O$), 95 (70, $C_7H_3D_4$), 94 (90, $C_7H_4D_3$)

Phthalyl Alcohol-3,4,5,6,1',1',2',2'-d_8 (**41d**)

The diol **41d** was prepared by reduction of 100 mg (0.65 mmol) of phthalic anhydride-d_4 (**40b**) with 30 mg (0.71 mmol) of lithium aluminum deuteride (Roth, 99 atom % D) suspended in tetrahydrofuran. The same purification procedure as for diol **41c** was followed to give 80 mg (88%) of colorless crystals, 96.8 ± 1 atom % D.

Physical Data for **41d**

mp: 62-64°

ir ($CHCl_3$) cm^{-1}: 3620 (s), 3330 (vs)

^1H nmr, 60 MHz ($CDCl_3$): no detectable signals could be observed (standard: 1,2-dichloroethane, 2H)

mass spectrum (m/e): 128 ($M-18^+$ C_8D_8O)

1,3-Dihydroisobenzofuran-2,2,3,4,5,6,7,7-d_8 (Phthalan **24d**)

The phthalan **24d** was prepared following the procedure described for the per-protio analogue **24a**. Thus from 67 mg (0.45 mmol) of phthalyl alcohol-d_8 was obtained 50 mg (86%) of colorless oil, 96.8 ± 1 atom % D.

Physical Data for **24d**

bp: 80-110° (10 Torr)

ir (neat) cm^{-1}: 2280 (w), 2190 (m), 2180 (m), 2100 (m), 2070 (w), 1590 (w), 1410 (w), 1370 (w), 1360 (w), 1300 (m), 1200 (m), 1180 (w), 1110 (w), 1090 (w), 1045 (vs), 1030 (m), 980 (m), 860 (w), 810 (s), 730 (s), 660 (w), 568 (vs)

^{1}H nmr, 100 MHz ($CDCl_3$): negative (standard: 1,2-dichloroethane, 2H)

mass spectrum (m/e): 128 (100, M^+ C_8D_8O), 126 (20, C_8D_7O), 124 (40, C_8D_6O), 98 (80, C_7D_7)

Syn-Cyclobutandiene Dimer-$\underline{h}_8$ (29)

A 250-ml, round bottomed flask with four vertical necks was fitted with a mechanical stirrer, gas inlet, Claisen tube and gas bubbler (Note 1). A solution of 1.0 g (5.2 mmol) of cyclobutadiene-$\underline{h}_4$-iron tricarbonyl[77,78] in 10 ml of acetone and 2 ml of water was transferred to the flask (Note 2). The golden mixture was cooled to 0°C and with violent stirring 10-12 g (18-22 mmol) of powdered ceric ammonium nitrate was added in 0.5 g portions over 30 min. The reaction mixture was further stirred at 0°C until no more CO was evolved (30 min), and then was poured into 120 ml of ice-cold brine, extracted with three 30-ml portions of n-pentane, washed with water and dried over anhydrous Na_2SO_4 in the cold (5°C). The bulk of the solvent was removed at atmospheric pressure in a spinning-band distillation column (oil bath: 40°C) and the oily residue was triturated with 2 ml of n-pentane, filtered and purified by preparative glc (Note 3). The product was collected at liquid N_2 temperature to give upon warming to room temperature a colorless, clear mobile oil identical in all respects with syn-tricyclooctadiene.[51]

Physical Data for 29

bp: 45° (50 Torr)

ir (neat) cm^{-1}: 3130 (w), 3040 (m), 2980 (m), 1550 (w), 1290 (s), 1180 (m), 1160 (w), 1000 (w), 955 (m), 815 (m), 790 (vs), 745 (m), 740 (m), 445 (m)

^{1}H nmr, 60 MHz ($CDCl_3$) δ: 3.85 (s, 4), 6.20 (s, 4)

mass spectrum (m/e): 104 (M^+ C_8H_8)

Notes

1. The reaction was carried out in a well ventilated fume hood.
2. The apparatus had been previously flushed with nitrogen and was kept throughout the reaction under a static nitrogen atmosphere.
3. Glc (50 µl): UC-W98; injection port, 60-70°C; oven, isothermal, 50-60°C; detector, 50°C; carrier gas, helium; flow rate, 60 ml per min.

Syn-Cyclobutadiene Dimer-d_8 (**45**)

The per-deuterio compound was prepared in the same manner as that described above for the per-protio analogue **29**. Starting with cyclobutadiene-d_4-iron tricarbonyl (1.0 g), a clear, colorless mobile oil was obtained after glc purification under the same conditions as for the per-protio compound.

Physical Data for **45**

bp: 48° (40 Torr)

ir (neat) cm^{-1}: 2278 (w), 2250 (m), 2225 (w), 1490 (w), 1152 (w), 1150 (w), 1142 (m), 1028 (w), 1008 (m), 855 (w), 840 (m), 769 (s), 722 (w), 710 (m), 668 (vs), 628 (s), 612 (m), 590 (m), 382 (vs)

^{1}H nmr, 60 MHz ($CDCl_3$): negative (standard: p-di-tert-butylbenzene, aromatic 2H)

mass spectrum (m/e): 112 (M^+ C_8D_8)

1,6-Bis-(methoxycarbonyl)-tetracyclo[4.4.0.$0^{2,5}$.$0^{7,10}$]-deca-3,8-diene-2,3,4,5,7,8,9,10-d_8 (42)

A 500-ml, round-bottomed flask with three vertical necks was fitted with a mechanical stirrer, gas inlet, Claisen tube and gas bubbler (Note 1). Under nitrogen, 2.94 g (15.0 mmol) of cyclobutadiene-d_4-iron tricarbonyl (33), 852 mg (5.9 mmol) of dimethyl acetylenedicarboxylate, 54 ml of acetone and 6 ml of hexane were transferred to the flask. The resulting solution was cooled in an ice-water bath and with violent stirring, 27 g (49.2 mmol) of finely powdered ceric ammonium nitrate was added in small portions over a 20-min period.[81] The reaction mixture was stirred for an additional 30 min, then poured into an ice-cold mixture of 300 ml of brine and 75 ml of water, and extracted with six 50-ml portions of ether. The combined extracts were washed with water (3 x 50 ml) and brine (3 x 50 ml) and then dried over anhydrous $MgSO_4$. Ether removal in vacuum gave 1.79 g of a light-brown oil. The pure product was isolated by column chromatography (Note 2) affording 790 mg (52%) of colorless solid, 98 ± 1 atom % D.

Physical Data for 42

mp: 64-65° (n-pentane)

ir ($CHCl_3$) cm^{-1}: 1720 (vs)

^1H nmr, 60 MHz ($CDCl_3$) δ: 3.60 (s, 6) (standard: maleic anhydride, 2H)

mass spectrum (m/e): 254 (M^+ $C_{14}H_6D_8O_4$)

Notes

1. The toxicity of the iron carbonyls and evolved carbon monoxide require this reaction to be carried out in a well ventilated hood.
2. The reaction mixture was first chromatographed on 30 g of silica gel, eluting with dichloromethane, to yield 700 mg of solid crude product and 356 mg of brownish oily mixture. The oil was rechromatographed on 30 g of silica gel, eluting with dichloromethane, to give an additional 197 mg of crude crystalline product. The combined crude product was further purified by column chromatography on 10 g of silica gel eluting with 10% ether-hexane and yielding the chromatographically pure product as a colorless solid.

1,6-Bis-(hydroxymethyl)-tetracyclo[4.4.0.$0^{2,5}$.$0^{7,10}$]deca-3,8-diene-2,3,4,5,7,8,9,10-d_8 (43)

A solution of 790 mg (3.10 mmol) of the diester 42 in 70 ml of tetrahydrofuran was placed in a 200-ml, oven-dried, round-bottomed flask fitted with a reflux condenser. While stirring at room temperature and maintaining an argon atmosphere, 6.4 ml (6.85 mmol) of lithium aluminum hydride in tetrahydrofuran was added dropwise (Note 1). The resulting suspension was further stirred at 50°C for 2 h to give a colorless transparent solution which was quenched with 1.0 ml of water in 20 ml of tetrahydrofuran. The mixture was stirred at room temperature for 5 h, filtered through a Celite pad and the inorganic salts washed with seven 20-ml portions of warm tetrahydrofuran (Note 2). The combined filtrates were evaporated to dryness in vacuum to afford 616 mg (99%) of colorless powder, 98 ± 1 atom % D (Note 3).

Physical Data for **43**

mp: 157-159° (sublimed at 60-80°, 25 mTorr)

ir ($CHCl_3$) cm^{-1}: 3620 (s), 3330 (vs)

^1H nmr, 60 MHz ($CDCl_3$-DMSO-d_6) δ: 3.60 (s, 4) (standard: maleic anhydride, 2H)

mass spectrum (m/e): 180 ($M-18^+$ $C_{12}H_4D_8O$)

Notes

1. The temperature of the reaction mixture was kept between 40 and 50°C due to the labile nature of both starting material and product.
2. The lithium and aluminum salts were transferred to the reaction flask and then were triturated with 20 ml of warm tetrahydrofuran, filtered and this

sequence repeated a total of seven times.

3. This compound was sufficiently pure to be used in the next step. It was dried in vacuum by azeotropic removal of water with anhydrous benzene.

12-Oxa-pentacyclo[4.4.3.0.0.^{2,5}.0^{7,10}]trideca-3,8-diene-2,3,4,5,7,8,9,10-d_8 (**44**)

To a 250-ml, three-necked, round-bottomed flask fitted with a magnetic stirring bar, 50-ml dropping funnel and two serum caps (Note 1) were transferred 1.10 g (1.32 ml, 7.82 mmol, 2.5 equiv) of 2,2,6,6-tetramethylpiperidine and 14 ml of anhydrous tetrahydrofuran. The resulting solution was cooled with stirring to -30 to -35°C with a dry ice-acetone bath and 5.3 ml (6.83 mmol, 2.2 equiv) of *n*-butyllithium in hexane added dropwise. The mixture was allowed to warm to room temperature and then cooled to -80°C. A solution of 616 mg (3.10 mmol, 2.0 equiv) of diol **43** in 10 ml of tetrahydrofuran and 10 ml of hexamethylphosphoric triamide was added dropwise with stirring. The reaction mixture was gradually warmed to ambient temperature to give a light yellow solution (Note 2). While stirring vigorously, 1.19 g (9.96 mmol, 3.2 equiv) of *p*-toluenesulfonyl chloride (Note 3) in 22 ml of tetrahydrofuran was added dropwise into the solution over a period of 4 h. The golden reaction mixture was stirred for an additional 3 h, then poured into 565 ml of 4% aqueous NaCl and extracted with ether (6 x 50 ml). The combined etheral extracts were washed with 15% aqueous NaCl (3 x 50 ml) and with 50 ml of brine, and then dried over anhydrous $MgSO_4$. Removal of the solvent on the rotary evaporator gave a lightly colored oil which was purified by column chromatography (Note 4) to afford 403 mg (72%) of colorless solid, 98 ± 1 atom % D.

Physical Data for **44**

mp: 45-46°

^{1}H nmr, 60 MHz ($CDCl_3$) δ: 3.59 (s, 4) (standard: maleic anhydride, 2H)

mass spectrum (m/e): 180 (M^+ $C_{12}H_4D_8O$)

Notes

1. All the apparatus used for this reaction was dried in the oven at 120°C for 48 h, assembled and allowed to cool either in a desiccator or under a stream of argon. A static argon pressure was maintained throughout the experiment.
2. Hexamethylphosphoric triamide solidified in the cold reaction mixture and warming to approximately -40°C was necessary to allow stirring to be resumed.
3. The commercial grade product (Baker) was used without

further purification.

4. The reaction mixture was percolated through 20 g of silica gel with dichloromethane yielding 345 mg of crude solid product and 143 mg of an oily mixture. The oil was chromatographed on 13 g of silica gel eluting with 10% ether-hexane to afford 97 mg of additional solid. The combined crude product was then chromatographed on 20 g of silica gel eluting with 8% ether-hexane to provide pure **44**.

12-Oxa-tetracyclo[4.4.3.0.0^{2,5}]trideca-3,7,9-triene-2,3,4,5,7,8,9,10-d_8 (**31b**)

A magnetically stirred solution of 403 mg (2.24 mmol) of the pentacyclic ether **44** in 9 ml of toluene was heated to 105°C under argon for 3 h (Note 1). The mixture was allowed to cool to room temperature and was subjected to column chromatography (Note 2) to give 368 mg (91%) of pure product which was bulb-to-bulb distilled (55°, 0.3 Torr) to afford 343 mg (85%) of **31b** as colorless solid, 97.9 ± 0.2 atom % D.

Physical Data for **31b**

mp: 37-38°

uv (methanol): λmax 264 nm (ε = 2500)

ir (neat) cm^{-1}: 2960 (m), 2925 (m), 2860 (s), 2320 (w), 2280 (w), 2245 (w), 2220 (w), 1570 (w), 1475 (w), 1465 (w), 1365 (w), 1248 (m), 1210 (w), 1180 (w), 1170 (w), 1140 (w), 1120 (w), 1083 (s), 1074 (s), 1010 (s), 990 (w), 930 (s), 898 (m), 760 (m), 750 (m), 732 (m), 694 (m), 650 (w), 640 (w), 610 (vs), 585 (vs), 495 (w), 370 (m)

^{1}H nmr, 60 MHz ($CDCl_3$) δ: 3.48 and 3.77 (dd, J = 9 Hz, 4) (standard: maleic anhydride, 2H)

mass spectrum (m/e): 180 (10, M^+ $C_{12}H_4D_8O$), 179 (5, $C_{12}H_3D_8O$), 178 (2, $C_{12}H_4D_7O$), 150 (100, $C_{11}H_2D_8$), 149 (40, $C_{11}HD_8$), 148 (60, $C_{11}H_2D_7$)

Notes

1. The reaction progress was followed by tlc and a clean conversion (95% or better) resulted after 2 h and 30 min.
2. The yellowish solution was adsorbed on 20 g of silica gel and eluted with hexane until toluene was removed, then the polarity was increased with 10% ether-hexane.

Cyclobutenedicarboxylic Anhydride (25)

This compound was prepared by benzophenone-sensitized photoaddition of acetylene and maleic anhydride according to the known procedure.[52] Alternatively it can be prepared from *cis*,*cis*-muconic anhydride.[89]

Physical Data for 25

mp: 94-95° (benzene-cyclohexane, sublimed: 60-65°, 0.3 Torr)

ir ($CHCl_3$) cm^{-1}: 2990 (w), 1865 (s), 1780 (vs), 1605 (w), 1270 (w), 1255 (m), 1230 (s), 1160 (m), 1070 (vs), 855 (s), 610 (w)

^1H nmr, 60 MHz ($CDCl_3$) δ: 4.19 (s, 2), 6.52 (s, 2)

mass spectrum (m/e): 80 (15.0, M-44$^+$ C_5H_4O), 52 (100.0, C_4H_4), 51 (29.0, C_4H_3), 50 (25, C_4H_2)

Maleic Anhydride-2,3-d_2 (46)

To 4.26 g (30.0 mmol) of dimethyl acetylenedicarboxylate in 100 ml of ethyl acetate contained in a 250-ml Erlenmeyer flask was added 200 mg of hydrogen-free Pd on charcoal (Note 1). The stirred suspension was reduced with D_2 at 25-30°C and 1 atm for 30 min and then was filtered and concentrated in vacuum to give 4.38 g (100%) of colorless oil. This crude material was heated at reflux for 4 h with 10% NaOD in 75 ml of deuterium oxide (Note 2). The resulting solution (Note 3) was allowed to cool to room temperature and subjected to continuous extraction with ether (Note 4). The last three extracts were combined, the solvent removed on the rotary evaporator and the resulting solid recrystallized from ether to give 1.82 g (50%) of maleic acid-2,3-$\underline{d}_2$ as colorless crystals, mp 135-136°.

To a stirred suspension of 1.34 g (11.3 mmol) of the above maleic acid-2,3-$\underline{d}_2$ in 15 ml of ether under argon was added 2.8 g (1.90 ml, 13.5 mmol, 1.2 equiv) of trifluoroacetic anhydride. The reaction mixture was stirred at room temperature for 30 min and the solvent removed in vacuum to give a colorless solid which contained a residual amount of trifluoroacetic anhydride that was removed by repeated codistillation with carbon tetrachloride. The residue was subjected to sublimation (60-65°, 20 Torr) to afford 1.03 g (90%) of colorless maleic anhydride-2,3-$\underline{d}_2$ (**46**),[56] 98 ± 1 atom % D.

Physical Data for **46**

mp: 56-57°

^{1}H nmr, 60 MHz ($CDCl_3$) δ: negative (standard: cyclobutenedicarboxylic anhydride, 2H)

mass spectrum (m/e): 108 (M^+ $C_4D_2O_3$)

Notes

1. Hydrogen-free 5% Pd on charcoal was prepared by

Mozingo's method.[90]

2. Sodium hydroxide-d was made from 4.0 g of freshly cut sodium and 75 ml of deuterium oxide (99.8 atom % D). An ice-water bath and an inert atmosphere was used.

3. The solution presumably contains disodium salts of acetylene dicarboxylic acid (mp 180-187° dec), maleic acid-2,3-d_2 (mp 134-136°), fumaric acid-2,3-d_2 (mp 299-300°) and succinic acid-d_4 (mp 187-190°).

4. The pH of the aqueous solution was adjusted gradually from 4.5 to <1.0 over a period of 24 h by adding concentrated HCl (indicators: pH 12 to 4.5, indicator paper; 4.5-3.0, bromophenol blue; 3.0-1.2, thymol blue; 1.2 to <1.0, thymol blue).

Cyclobutenedicarboxylic Anhydride-d_4 (47)

A pyrex photolysis flask was charged with a solution of 520 mg (4.81 mmol) of maleic anhydride-d_2 and 350 mg of benzophenone in 12 ml of acetone (Note 1) and then cooled to -78 to -80°C with a dry ice-methanol bath under a slow stream of nitrogen (Note 2). Acetylene-d_2[55] was slowly bubbled into the solution for 1.5 h (Note 3); the acetylene generator was disconnected and a slow stream of nitrogen was passed through the solution for 2 min (Note 4) then both inlet and outlet valves of the reaction flask were closed, isolating the system. The pressure in the flask was monitored by a mercury manometer. The cold mixture (Note 5) was photolyzed for 1.5 h with a medium pressure Hanovia mercury lamp (450 W).[52] The yellowish reaction mixture was warmed to room temperature in a well-ventilated hood and most of the acetylene escaped. Removal of solvent using the rotary evaporator followed by bulb-to-bulb distillation (85-90°C, 0.6 Torr, trapped at dry ice temperature) gave a colorless solid (Note 6). Recrystallization from benzene-cyclohexane provided 334 mg (50%) of **47** as colorless needles, mp 91-94°C, 98.5 ± 0.5 atom % D.

Physical Data for **47**

mp: 94-95° (benzene-cyclohexane, sublimed: 70°, 0.6 Torr)

ir ($CHCl_3$) cm^{-1}: 1855 (s), 1790 (vs), 1265 (m), 1230 (s), 1155 (w), 1000 (w), 970 (s), 905 (w), 890 (s), 850 (w), 810 (m), 710 (w), 610 (m), 550 (m)

^1H nmr, 60 MHz ($CDCl_3$) δ: negative (maleic anhydride-$\underline{h}_2$ as standard, 2H).

mass spectrum (m/e): 84 (11.5, $M-44^+$ C_5D_4O), 56 (100.0, C_4D_4), 55 (10.0, C_4HD_3), 54 (29.5, C_4D_3, $C_4H_2D_2$), 53 (3.0, C_4HD_2, C_4H_3D), 52 (24.6, C_4D_2, C_4H_2D, C_4H_4)

Notes

1. Reagent grade acetone was dried with K_2CO_3 and distilled.

2. Nitrogen gas was bubbled through the cold solution for 20 min.

3. Acetylene-$\underline{d}_2$ was generated from 5.5 ml of deuterium oxide (99.8 atom % D) and calcium carbide. The acetylene generator was kept at ice-bath temperature while deuterium oxide was added dropwise over a 40 min period. It was shaken after each drop was added to provide a new surface for the next drop. The generator was then warmed to room temperature and was kept connected to the system for further 30 min by which time the generation of acetylene-$\underline{d}_2$ became very slow. Dry nitrogen was then swept through the generator for 20 min to carry most of the remaining acetylene-$\underline{d}_2$ to the photolysis flask.

The method described provides 50-60% of the theoretical amount of acetylene-$\underline{d}_2$ and for this experiment approximately 30 times excess of acetylene over maleic anhydride-$\underline{d}_2$ should be present in the photolysis flask.

The brand of calcium carbide used affected both the deuterium content and yield of the generated acetylene. Fisher Scientific product (Mesh 20-30) was unsatisfactory since it contained very little active carbide. Baker and Adamson product (lump 3/8") was quite satisfactory when activated in the oven prior to use.

The generated acetylene-$\underline{d}_2$ was dried by passing through conc H_2SO_4, KOH pellets and soda lime, and its deuterium content was estimated in control experiments by trapping it with maleic anhydride-$\underline{h}_2$ as its photo-adduct which showed the following physical data.

mp: 93-95° (benzene-cyclohexane)

ir ($CHCl_3$) cm^{-1}: 1860 (s), 1785 (vs)

^1H nmr, 60 MHz ($CDCl_3$) δ: 4.10 (s, 2), 98 ± 0.5 atom % D (standard: p-di-tert-butylbenzene, 2H aromatic)

mass spectrum (m/e): 82 (14.0, $M-44^+$ $C_5H_2D_2O$), 54 (100.0, $C_4H_2D_2$), 53 (23.0, C_4HD_2, C_4H_3D), 52 (20.0, C_4H_2D, C_4H_4, C_4D_2), 51 (19.0, C_4HD, C_4H_3), 50 (8.0, C_4H_2, C_4D).

4. The slow stream of nitrogen was required at this stage to prevent the solution in the photolysis flask from being sucked into the inlet tube. Nitrogen by-passed the acetylene generator for this operation.

5. The solubility of acetylene in acetone at -78°C is very high and the volume of acetone increased over 100% when the acetylene had been bubbled.

6. The distillate consisted mainly of the desired photo-adduct and benzophenone (glc: UC-W98, SE-30).

α-Pyrone (30)

The method of Ban and co-workers[53] was preferred for the preparation of α-pyrone.

Physical Data for 30

bp: 60-70° (1 Torr)

ir (neat) cm^{-1}: 3130 (m), 3050 (w), 1790 (w), 1740 (vs), 1650 (w), 1630 (s), 1590 (w), 1550 (s), 1440 (m), 1380 (w), 1260 (s), 1190 (w), 1135 (s), 1095 (s), 1080 (s), 990 (w), 955 (m), 855 (m), 790 (vs), 730 (w)

^1H nmr, 100 MHz ($CDCl_3$) δ: 6.24 (m, 2), 7.39 (m, 2)

mass spectrum (m/e): 96 (40.5, M^+ $C_5H_4O_2$), 95 (8.1, $C_5H_3O_2$), 68 (61.5, C_4H_4O), 42 (16.3, C_2H_2O), 40 (32.5, C_2O), 39 (100.0, C_3H_3)

3-Oxoglutaric Anhydride (49)

To an ice-cold mixture of 50 ml of acetic acid and 14.0 g (0.13 mol) of acetic anhydride under argon was added with stirring 10.0 g (68.4 mmol) of 3-oxoglutaric acid. The resulting suspension was stirred for 5 min and allowed to warm to room temperature, and then was further stirred for 1.5 h (Note 1). The mixture was cooled in ice and the precipitated anhydride was collected and washed several times with anhydrous ether. The filtrate was evaporated to dryness under reduced pressure to afford additional crystals. The yield of total anhydride **49** was 8.0 g (91%).[91]

Physical Data for **49**

mp: 133-134° (dec, tetrahydrofuran-ether, Note 2)

ir (tetrahydrofuran) cm^{-1}: 1797, 1740, 1643

^1H nmr, 60 MHz (Acetone-d_6) δ: 3.65 (s, 3), 5.35 (s, 1)

Notes

1. If a larger excess of acetic anhydride is used or the reaction time is prolonged, lower yields may be obtained due to acetylation of the desired product.
2. The product is decomposed to starting material if recrystallization is attempted from acetic acid.[92]

α-Pyrone-d_4 (**53**)

A solution of 2.05 g (16.0 mmol) of 3-oxo-glutaric anhydride in 10 ml of anhydrous tetrahydrofuran was treated with 10 ml (10.5 g, 172 mmol) of freshly prepared acetic acid-d (Note 1). The mixture was immediately evaporated to dryness in vacuum at room temperature. The above treatment was repeated four times requiring 15-20 min to evaporate the solution each time (Note 2).

The resulting 3-oxoglutaric anhydride-d_4 (**50**) was suspended in 40 ml of anhydrous carbon tetrachloride and in a nitrogen-purged, P_2O_5-dried glove bag was transferred 7.1 g (34 mmol) of freshly sublimed phosphorus pentachloride. The mixture was stirred under argon overnight at 45°C and the resulting brownish solution concentrated in vacuum. The residual carbon tetrachloride was codistilled with tetrahydrofuran and the residue, containing dichloride **51**, was then suspended in 30 ml of tetrahydrofuran and 7.80 g (42.6 mmol) of KI (Note 3) added. The mixture was stirred overnight under argon at room temperature to afford the corresponding iodide **52** which was reduced with 6 g of Zn dust (Note 4) and 10 ml of acetic acid-*d* at 0°C (Note 5). The residual solids were filtered, 200 ml of ether and 20 ml of water added, then the reaction mixture was neutralized with excess K_2CO_3, filtered and washed with two-50 ml portions of water and with 50 ml of brine. The ethereal solution was dried over anhydrous $MgSO_4$ and concentrated in vacuum to approximately 50 ml, then was percolated through 5 g of silica gel eluting with ether and the solvent evaporated at atmospheric pressure. The volatile part of the residue was collected at -80°C under reduced pressure giving 350 mg (20%) of yellow oil which was subsequently distilled (100°C, 20 Torr), 93.5 ± 0.5 atom % D.

Physical Data for **53**

bp: 80-90° (20 Torr)

ir (neat) cm^{-1}: 2315 (w), 2285 (w), 1730 (vs), 1675 (w), 1605 (w), 1590 (m), 1525 (s), 1300 (m), 1235 (m), 1070 (s), 1005 (w), 948 (w), 882 (w), 830 (m), 782 (m), 735 (m)

^{1}H nmr, 100 MHz ($CDCl_3$) δ: residual signals at 6.20, 6.32, 7.32 and 7.50 were observed (standard: p-di-tert-butylbenzene, 1H aromatic)

mass spectrum (m/e): 100 (72.3, M^+ $C_5D_4O_2$), 99 (11.4, $C_5HD_3O_2$), 98 (12.7, $C_5D_3O_2$), 72 (77.6, C_4D_4O), 71 (12.6, C_4HD_3O), 44 (43.4, C_2D_2O), 43 (7.3, C_2HDO), 42 (100.0, C_2DO), 41 (10.2, C_2HO), 40 (20.6, C_2O)

Notes

1. To 58 ml (62.7 g, 0.61 mol) of freshly distilled acetic anhydride was added dropwise with stirring 11.0 ml (12.2 g, 0.60 mol) of deuterium oxide (99.8 atom %D). The mixture was heated to refluxing for 2 h and then the product was fractionally distilled to give 70 g (95%) of acetic acid-d, bp 115-116°C, 98 ± 1 atom % D.
2. ^{1}H nmr analysis (Acetone-d_6) indicated the complete disappearance of the signals of the anhydride 49. p-Di-tert-butylbenzene (1H, aromatic) was used as standard.
3. Commercial KI was dried in vacuum over P_2O_5 for 24 h.
4. Activated Zn dust dried for 24 h over P_2O_5 in vacuum was used.

5. Acetic acid-d was added dropwise over 2 h, the mixture was then stirred at 0°C for 1 h and at room temperature overnight.

"It is best to do things systematically,
since we are only human, and disorder is
our worst enemy."

HESIOD (8th CENTURY B.-C.)

EXPERIMENTAL APPARATUS AND OPTIMUM CONDITIONS FOR THE PREPARATION OF MATRIX SAMPLES

This section contains a general description of the apparatus used for the matrix work performed in the course of this research and the data and basic principles that led this author to the selection, design and construction of the equipment. The parameters, figures and facts that have resulted in the achievement of reproducible experimental conditions are also reported.

Fortunately, the matrix isolation technique has been the subject of several books and numerous and authoritative recent reviews.[44,93-100] The book by Meyer[93] has a valuable chapter on experiment details, some of which are reproduced here for the sake of clarity only. The book edited by Hallam[94] focuses on vibrational spectroscopy. Of particular interest is the book by Cradock and Hinchcliffe[44] because these two authors describe very precisely and clearly the main factors governing the experimental conditions leading to reproducible results.

The matrix isolation method was developed in 1954 by Pimentel[33] to permit the leisurely spectroscopic study of extremely reactive species.[33] In essence, the method involves the trapping at high dilution of the reactive species or its photoprecursor in an inert environment at cryogenic temperatures. Under such conditions, molecules that normally have short lifetimes can be preserved indefinitely.

A block diagram of the equipment needed for cryogenic studies is represented in Figure 22.

The matrix isolation technique necessarily involves a combination of several technologies. The low temperatures needed to form rigid matrices require cryogenic technology, which in turn involves the use of high vacuum, otherwise low temperatures cannot be conveniently maintained. Thus only spectroscopic methods can be used to study matrix-isolated species.

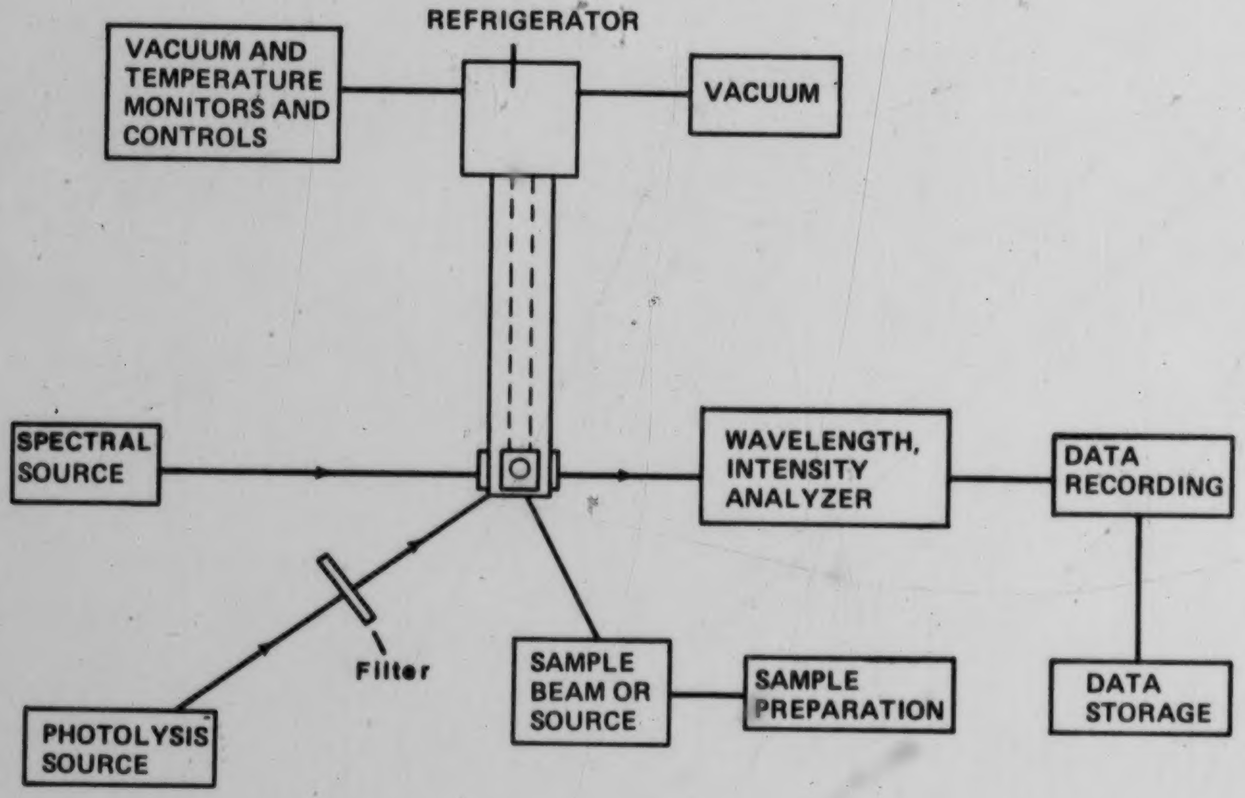

REFRIGERATOR
VACUUM AND TEMPERATURE MONITORS AND CONTROLS
VACUUM
SPECTRAL SOURCE
WAVELENGTH, INTENSITY ANALYZER
DATA RECORDING
Filter
SAMPLE BEAM OR SOURCE
SAMPLE PREPARATION
DATA STORAGE
PHOTOLYSIS SOURCE

FIGURE 22. Block Diagram of Equipment Needed for Cryogenic Studies.

APPARATUS

Cryostat and Accessories

Matrices are formed by the condensation of a gas beam on a cold target or window. The beam contains a very dilute solution of the "guest" species in a "host" matrix gas. Only the rare gases and molecular nitrogen were both chemically inert and sufficiently transparent in the infrared to be suitable as host matrix materials in the present study. The formation of matrices from the rare gases requires cooling of the target to temperatures between 9°K (neon) and 55°K (xenon). Temperatures below 77°K, the lowest temperature used in conventional chemistry, can be reached with safety using liquid helium and a double-Dewar cryostat[101] or a continuous flow cryostat.[102] In these cryostats the target to be cooled is mounted on the bottom surface of an inner chamber. Liquid helium is transferred into this chamber by pressurizing a storage Dewar with helium gas, thereby forcing the refrigerant into the interior of the cryostat. The cold target is separated from the atmosphere by an evacuated area. The vacuum (vide infra) must be high enough to prevent heat leakage.*

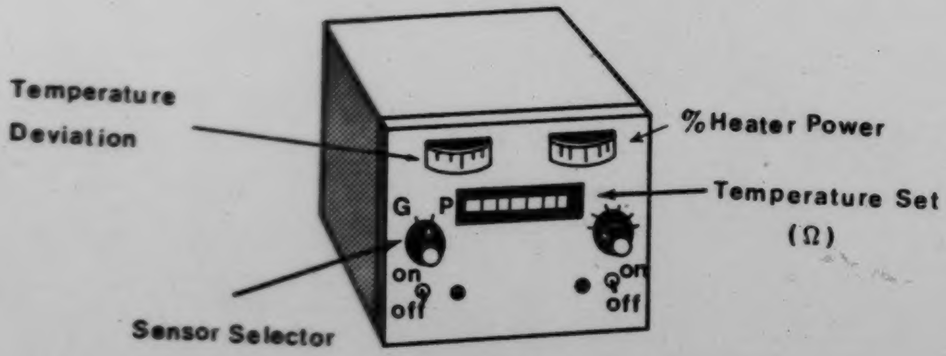
---

* This criterion is usually met at approximately 10^{-4} Torr.

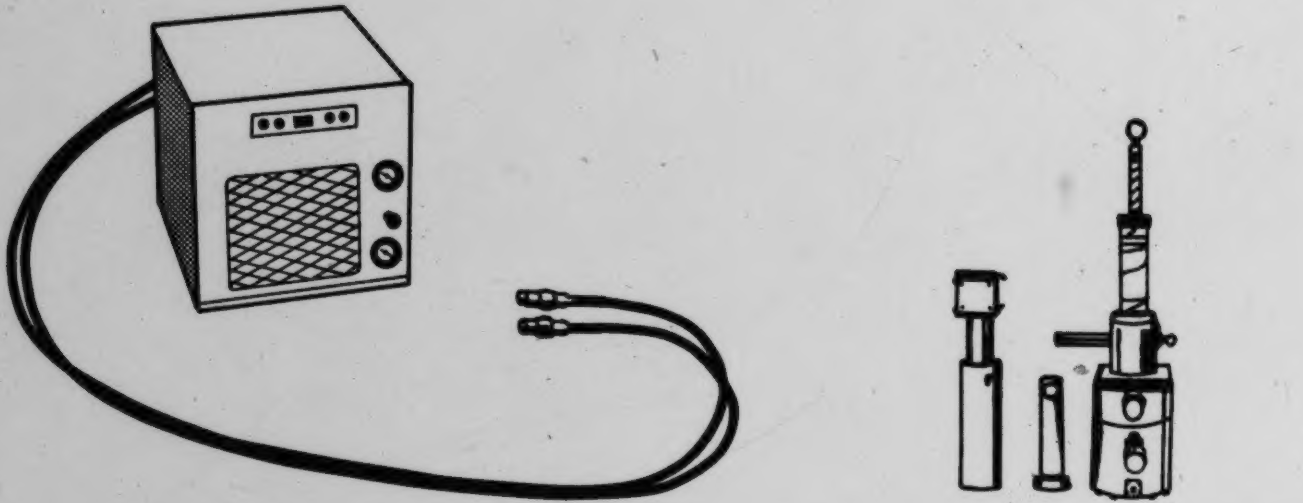
An alternative way of achieving low temperatures without using liquid helium is by means of a closed-cycle microrefrigerator.[102a,103] These systems are adequate for most matrix work and for this research, a Displex microrefrigerator, Model CSW-202 made by Air Products[102a] was chosen (Figure 23). With this system, temperatures of 7-8°K were readily reached and maintained for days at a time, greatly extending the time-scale of the matrix-isolation experiments.

The temperature of the cold end of the Displex was measured using an iron-doped gold (0.07 Atom %) vs. chromel termocouple. The e.m.f. produced by the thermocouple was monitored on a Digital Microvoltmeter, Model DRC-5 made by Lake Shore Cryotronics.[104] Temperatures above 7-8°K were achieved by adjusting the rate of heating provided by a small heater surrounding the cold end until it was greater than the rate of cooling. The desired temperatures were maintained using an Air

MODEL APD-C



Automatic Temperature Controller



Displex CS-202 Air-Cooled Compression Unit with 10-ft Flexible Interconnecting Lines

Displex CS-202 Expansion Unit With Optical Vacuum Shroud and Radiation Shield

FIGURE 23. Air Products Displex® CSW-202 Closed Cycle (Helium Gas) Microrefrigerator.

Products Automatic Temperature Controller, Model APD-C with germanium and platinum sensors. These sensors provide the temperature controller with input generating heater current proportional to the difference between the desired temperature (set on a dial) and the measured temperature. Temperature regulation to 0.1°K was easily obtained.

The Displex expansion unit (Figure 23) was mounted on the base plate of an horizontal slide which itself was mounted on a vertical slide, so that the optical center of the target could be moved precisely in the vertical and horizontal directions. This facilitated the alignment of the target with respect to the infrared spectrophotometer. The entire cryogenic assembly, including the Displex compression unit (Figure 23), the temperature monitor and controller, and a vacuum monitor (NRC 856 Cold Cathode Gauge Control), was mounted on a carriage with soft-rubber doughnut wheels to allow easy access of the unit to the spectrophotometer.

High Vacuum Pumping System[105]

The maintenance of low temperatures for the formation of solid matrices from the rare gases requires the use of high vacuum for insulation (*vide supra*). This makes it relatively easy to build up matrices by condensation of the inert gases on the cooled target. However, the cold surface will also act as a cryotrap for air from any leaks and for substances within the system which evaporate as the pressure is lowered. Evacuation of the apparatus to a pressure of about 10^{-6} Torr ensures the detection of appreciable leaks which can then be sealed, and removes traces of gases and vapors adsorbed on metal or glass surfaces. To attain pressures in this range, it is necessary in matrix work to use a two-stage pumping system. A common arrangement

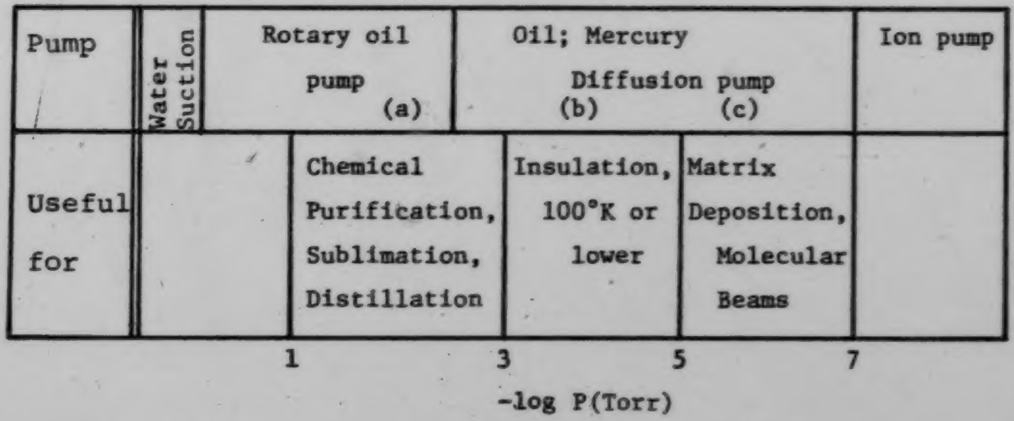
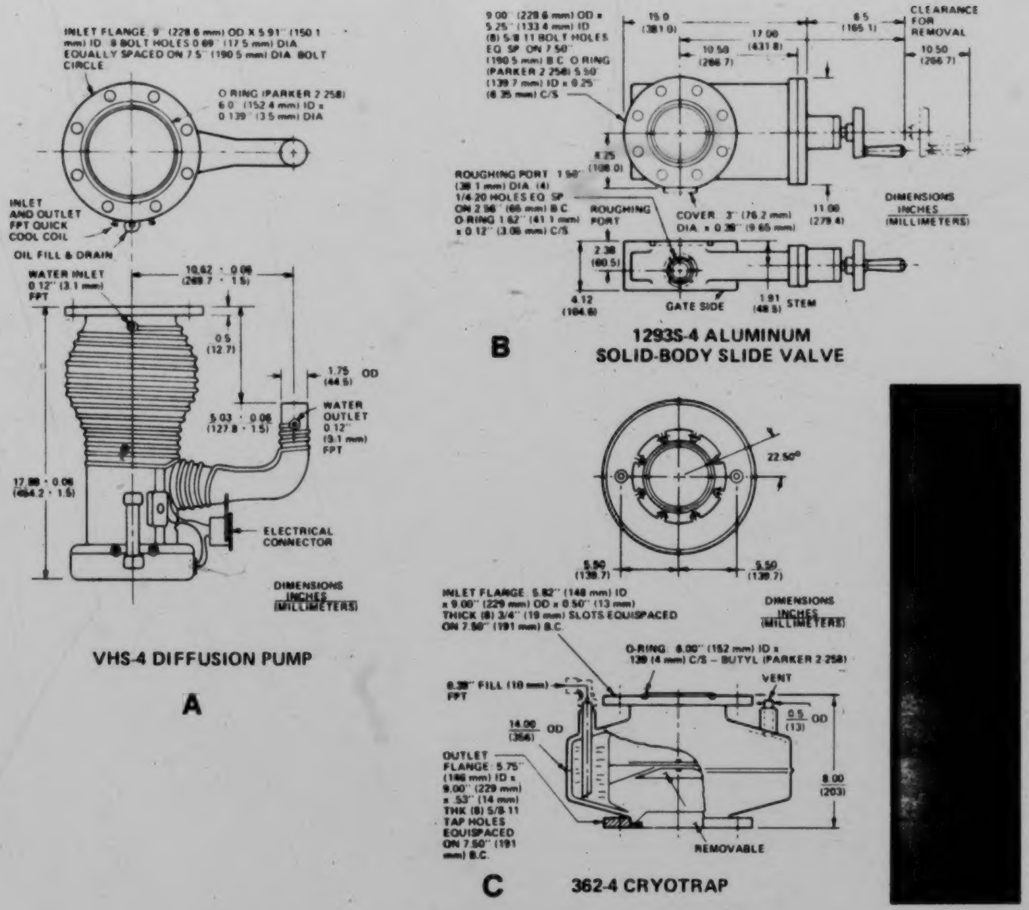

Pump
Water Suction
Rotary oil pump (a)
Oil; Mercury Diffusion pump (b) (c)
Ion pump
Useful for
Chemical Purification, Sublimation, Distillation
Insulation, 100°K or lower
Matrix Deposition, Molecular Beams
1
3
5
7
-log P(Torr)

FIGURE 24. Pressure Ranges Necessary for (a) Preparation and Purification of Chemicals, (b) Insulation of Cryogenic Vessels, and (c) Production of Molecular Beams.[93]

is that of a mechanical pump, which can provide an ultimate pressure of the order of 10^{-3} Torr, backing an oil-diffusion pump. The latter reduces the ultimate pressure to 10^{-6} Torr and increases the speed of pumping near the lower pressure limit of the rotary pump (Figure 24). For the work described here, a Varian VHS-4 oil diffusion pump (Figure 25A) and a 10-CFM (300-liter/min) Welch 1376-B mechanical pump were selected. The diffusion pump was connected to a stainless steel main manifold (Figure 26), built and designed in this Department, through a Varian 1293S-4 (Figure 25B) pneumatically operated slide valve (V_1). A Varian 362-4 Long-life Cryotrap (liquid nitrogen) was installed to protect the target from residual gases from the oil diffusion pump. The main valve V_1 allowed the diffusion pump to be isolated from the system so that the pump could be continuously operated while the main manifold and its connections were open, were being prepared for re-pumping or were being evacuated ("roughed") with the mechanical pump (Figure 26).

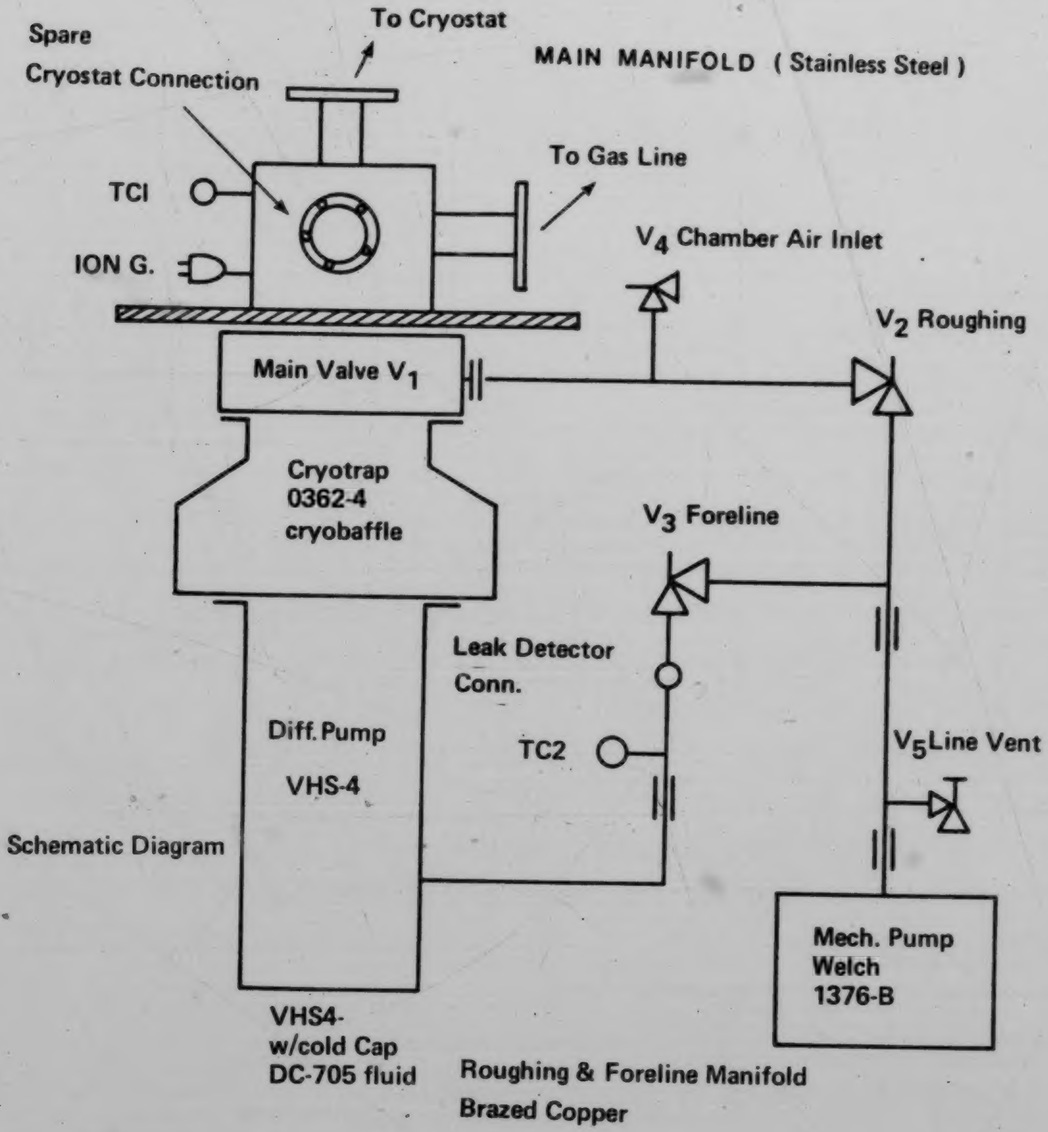
The three Varian components, diffusion pump, cryotrap and slide valve (Figure 25), were factory assembled and cart mounted to give a compact unit with a pumping speed of 460 liters/sec (air) and an ultimate pressure range of 10^{-7} Torr (Figure 27).

The thermocouple vacuum gauge TC1 (Figure 26)


INLET FLANGE 9" (228.6 mm) OD X 5.91" (150.1 mm) ID 8 BOLT HOLES 0.69" (17.5 mm) DIA EQUALLY SPACED ON 7.5" (190.5 mm) DIA BOLT CIRCLE
O RING (PARKER 2 258) 6.0" (152.4 mm) ID x 0.139" (3.5 mm) DIA
INLET AND OUTLET FPT QUICK COOL COIL
OIL FILL & DRAIN
WATER INLET 0.12" (3.1 mm) FPT
10.62 ± 0.06 (269.7 ± 1.5)
0.5 (12.7)
1.75 (44.5) OD
5.03 ± 0.06 (127.8 ± 1.5)
WATER OUTLET 0.12" (3.1 mm) FPT
17.88 ± 0.06 (454.2 ± 1.5)
ELECTRICAL CONNECTOR
DIMENSIONS INCHES (MILLIMETERS)
VHS-4 DIFFUSION PUMP
A
9.00" (228.6 mm) OD x 5.25" (133.4 mm) ID (8) 5/8 11 BOLT HOLES EQ SP ON 7.50" (190.5 mm) B.C. O RING (PARKER 2 258) 5.50" (139.7 mm) ID x 0.25" (6.35 mm) C/S
15.0 (381.0)
17.00 (431.8)
10.50 (266.7)
6.5 (165.1)
CLEARANCE FOR REMOVAL
10.50 (266.7)
4.25 (108.0)
ROUGHING PORT 1.50" (38.1 mm) DIA (4) 1/4-20 HOLES EQ SP ON 2.56" (65 mm) B.C. O-RING 1.62" (41.1 mm) x 0.12" (3.05 mm) C/S
ROUGHING PORT
COVER 3" (76.2 mm) DIA x 0.38" (9.65 mm)
11.00 (279.4)
DIMENSIONS INCHES (MILLIMETERS)
2.38 (60.5)
4.12 (104.6)
GATE SIDE
1.91 (48.5) STEM
B
1293S-4 ALUMINUM SOLID-BODY SLIDE VALVE
22.50°
5.50 (139.7)
5.50 (139.7)
INLET FLANGE 5.82" (148 mm) ID x 9.00" (229 mm) OD x 0.50" (13 mm) THICK (8) 3/4" (19 mm) SLOTS EQUISPACED ON 7.50" (191 mm) B.C.
DIMENSIONS INCHES (MILLIMETERS)
O-RING 6.00" (152 mm) ID x .139 (4 mm) C/S – BUTYL (PARKER 2 258)
0.38" FILL (10 mm) FPT
VENT
14.00 (356) OD
0.5 (13) OD
OUTLET FLANGE 5.75" (146 mm) ID x 9.00" (229 mm) x .53" (14 mm) THK (8) 5/8-11 TAP HOLES EQUISPACED ON 7.50" (191 mm) B.C.
8.00 (203)
REMOVABLE
C
362-4 CRYOTRAP

varian

FIGURE 25. Varian VHS-4 Diffusion Pump (A), Varian 1293S-4 Air Operated Slide Gate Valve (B), and Varian 362-4 Long-Life Cryotrap (C).


Spare
Cryostat Connection
To Cryostat
MAIN MANIFOLD (Stainless Steel)
To Gas Line
TCI
ION G.
V_4 Chamber Air Inlet
V_2 Roughing
Main Valve V_1
Cryotrap
0362-4
cryobaffle
V_3 Foreline
Leak Detector
Conn.
Diff. Pump
VHS-4
TC2
V_5Line Vent
Schematic Diagram
Mech. Pump
Welch
1376-B
VHS4-
w/cold Cap
DC-705 fluid
Roughing & Foreline Manifold
Brazed Copper

VALVES

V_1 12955 5¼" ID A/O Slide Valve w/rough Port.

V_2, V_3 (2) 1252-1 1/8" A/O Bellows Sealed Forged Body

V_4 (1) 1252-3/4" A/O Bellows Sealed Forged Body

FIGURE 26. Schematic Representation of the High Vacuum Pumping System.

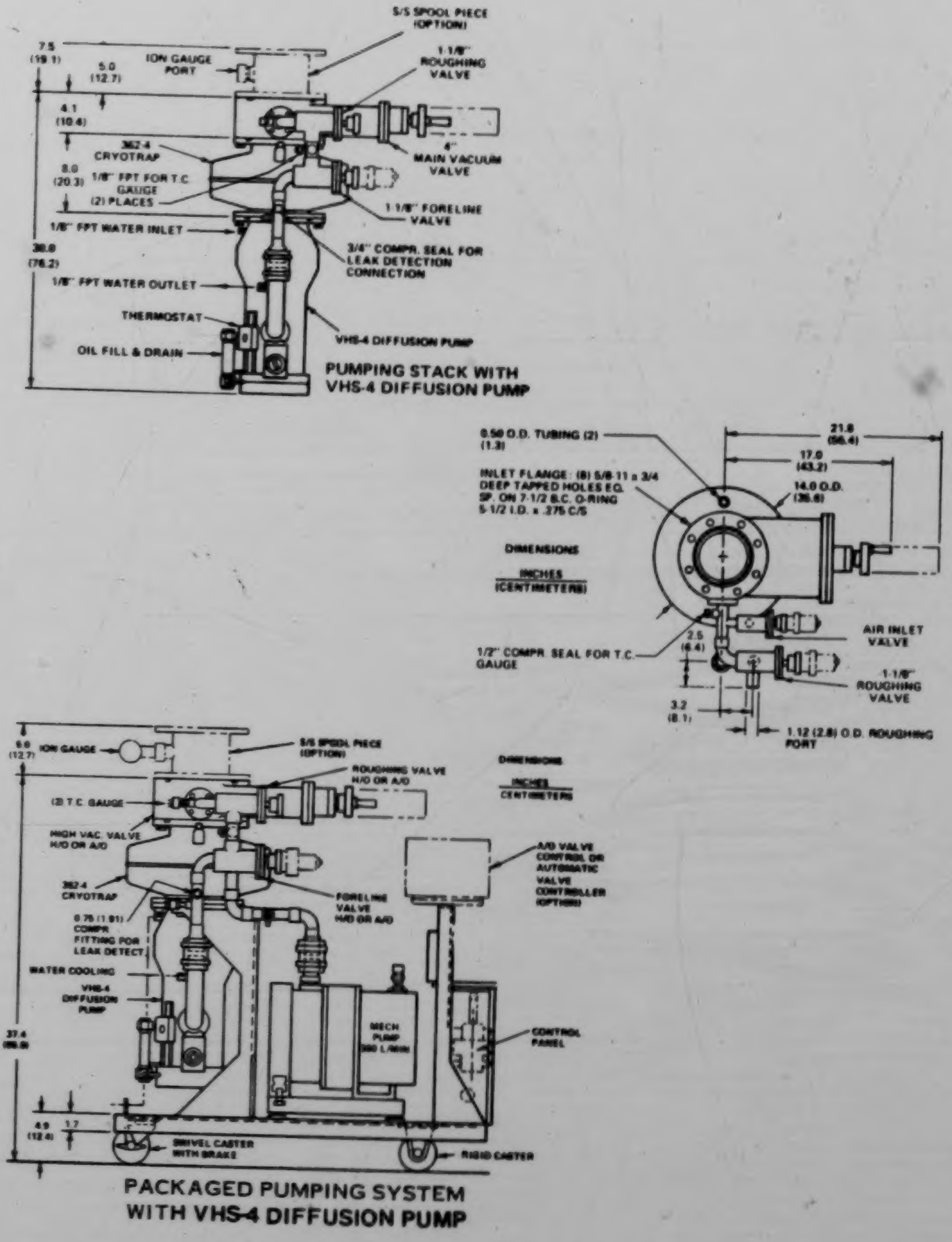
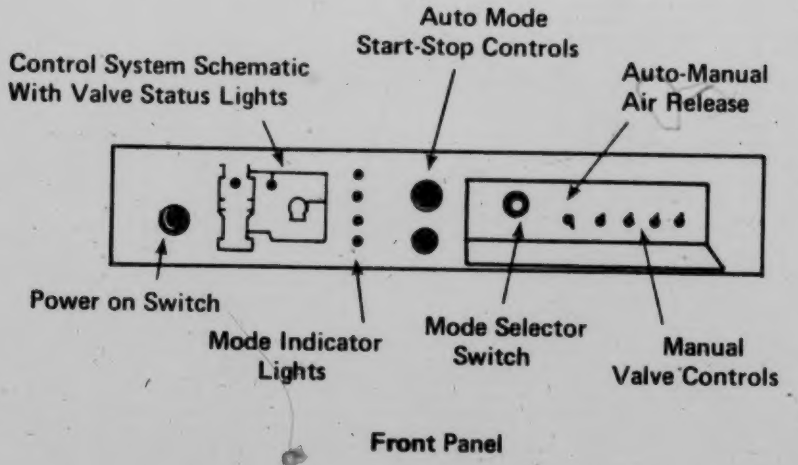

S/S SPOOL PIECE (OPTION)
7.5 (19.1)
5.0 (12.7)
ION GAUGE PORT
1-1/8" ROUGHING VALVE
4.1 (10.4)
362-4 CRYOTRAP
4" MAIN VACUUM VALVE
8.0 (20.3)
1/8" FPT FOR T.C. GAUGE (2) PLACES
1-1/8" FORELINE VALVE
1/8" FPT WATER INLET
30.0 (76.2)
3/4" COMPR. SEAL FOR LEAK DETECTION CONNECTION
1/8" FPT WATER OUTLET
THERMOSTAT
VHS-4 DIFFUSION PUMP
OIL FILL & DRAIN
PUMPING STACK WITH VHS-4 DIFFUSION PUMP
0.50 O.D. TUBING (2) (1.3)
21.8 (55.4)
17.0 (43.2)
INLET FLANGE: (8) 5/8-11 x 3/4 DEEP TAPPED HOLES EQ. SP. ON 7-1/2 B.C. O-RING 5-1/2 I.D. x .275 C/S
14.0 O.D. (35.6)
DIMENSIONS
INCHES / (CENTIMETERS)
AIR INLET VALVE
2.5 (6.4)
1/2" COMPR. SEAL FOR T.C. GAUGE
1-1/8" ROUGHING VALVE
3.2 (8.1)
1.12 (2.8) O.D. ROUGHING PORT
5.0 (12.7)
ION GAUGE
S/S SPOOL PIECE (OPTION)
ROUGHING VALVE H/O OR A/O
DIMENSIONS
INCHES / CENTIMETERS
(2) T.C. GAUGE
HIGH VAC. VALVE H/O OR A/O
A/O VALVE CONTROL OR AUTOMATIC VALVE CONTROLLER (OPTION)
362-4 CRYOTRAP
FORELINE VALVE H/O OR A/O
0.75 (1.91) COMPR FITTING FOR LEAK DETECT
WATER COOLING
VHS-4 DIFFUSION PUMP
MECH PUMP 500 L/MIN
37.4 (95.0)
CONTROL PANEL
4.9 (12.4)
1.7
SWIVEL CASTER WITH BRAKE
RIGID CASTER
PACKAGED PUMPING SYSTEM WITH VHS-4 DIFFUSION PUMP

FIGURE 27. Complete Cart Mounted High Vacuum Pumping System.

mounted in the main manifold indicated the progress of the initial stages of the evacuation of the apparatus (atmosphere to ~100 mTorr). For this "rough pumping" only the mechanical pump was used and valves V_1 and V_3 were closed and valve V_2 was open. During this time the diffusion pump continued to discharge gases into the sealed-off volume of foreline between the pump and valve V_3. The rising pressure in this volume was indicated by the thermocouple vacuum gauge TC2 and was not allowed to exceed 100 mTorr to avoid damage to the diffusion pump. This gauge also registered the backing pressure maintained by the mechanical pump in the foreline (Figure 26) when valves V_1 and V_3 were open and V_2 was closed (pressure in the main manifold <100 mTorr). The final stages of the evacuation were monitored by a hot ionization gauge (Bayard-Alpert) mounted in the main manifold.

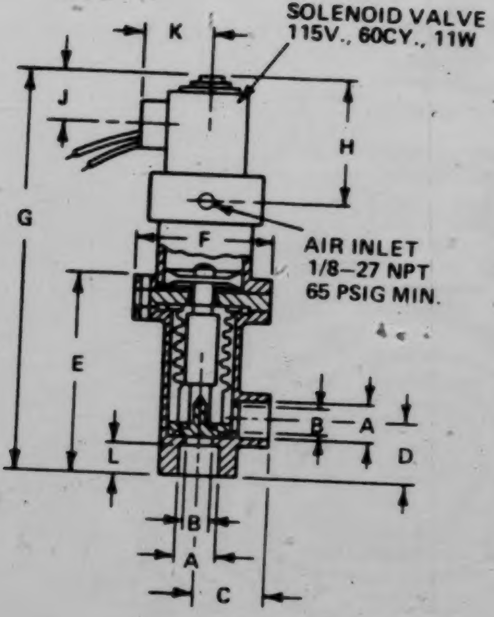
Operation of diffusion pumps at too high a pressure or sudden exposure to gases can lead to oil loss. In the system being used the consequences of oil spillage would have been so severe that the entire vacuum system would have required disassembly and cleaning. For this reason, the main high vacuum valves (V_1 to V_4) were equipped for automatic operation thus facilitating automatic "fail-safe" arrangements. A Varian 971-1016 Automatic Valve Control was installed in conjunction


Control System Schematic With Valve Status Lights
Auto Mode Start-Stop Controls
Auto-Manual Air Release
Power on Switch
Mode Indicator Lights
Mode Selector Switch
Manual Valve Controls
Front Panel

Varian 971-1016 Automatic Valve Control

with a Varian 843 Ratiomatic Ionization Gauge Control Unit. The latter signals the valve control when the pressure in the system is low enough to switch to the diffusion pump. This valve control provided automatic valve cycling of the vacuum system from atmosphere to high vacuum. The unit sequentially operated four (foreline, roughing, air release, and high vacuum) pneumatic valves (Figures 25B and 28) which were electrically actuated, with complete protection against operator error or power failure.

With this system, extraordinarily "clean" vacuums above the cryotrap were obtained and pressures of 10^{-7} Torr, desirable for matrix work, were feasible. Vaporization at low pressure of gases and vapors (particularly water) adsorbed on metal or glass surfaces (outgassing)


K
SOLENOID VALVE
115V., 60CY., 11W
J
H
G
F
AIR INLET
1/8–27 NPT
65 PSIG MIN.
E
B
A
L
D
B
A
C

1252 AIR-OPERATED VALVE (ANGLE)												
SIZE	A	B	C	D	E	F	G	H	J	K	L
3/8	3/8	1/4	1-13/32	1-3/16	4	2-3/4	8-3/64	2-5/8	1-1/32	1-7/16	5/8
1/2	1/2	3/8	1-13/32	1-3/16	4	2-3/4	8-3/64	2-5/8	1-1/32	1-7/16	5/8
3/4	3/4	5/8	1-13/32	1-3/16	4	2-3/4	8-3/64	2-5/8	1-1/32	1-7/16	5/8
1-1/8	1-1/8	1	2-1/32	1-11/16	5	3-3/8	9-27/64	2-5/8	1-1/32	1-7/16	15/16
1-5/8	1-5/8	1-1/2	2	1-11/16	5-7/16	4-1/4	10-11/64	2-5/8	1-1/32	1-7/16	3/4

FIGURE 28. Varian 1252 Air-Operated Solenoid Valves.

makes it impossible to reach such pressures. Outgassing was avoided by maintaining the vacuum system at low pressure, and so preventing the adsorption of polar substances. This is particularly important when a cryostat part is still cold since moisture condensed on a cold part desorbs very slowly. When it was necessary to break the vacuum, the system was filled with a dry gas.

The pumping system and accessories, including the spray-on sample preparation line to be described below, were mounted on a carriage with soft rubber doughnut wheels to facilitate the relocation of the unit. This carriage was stabilized at the appropriate location by raising on four jacks. The mechanical and diffusion pumps (the self-containing unit described above, Figure 27) were mounted on a subcarriage which was independently jacked to isolate the glass manifold (gas line) from the natural vibration of the entire system.

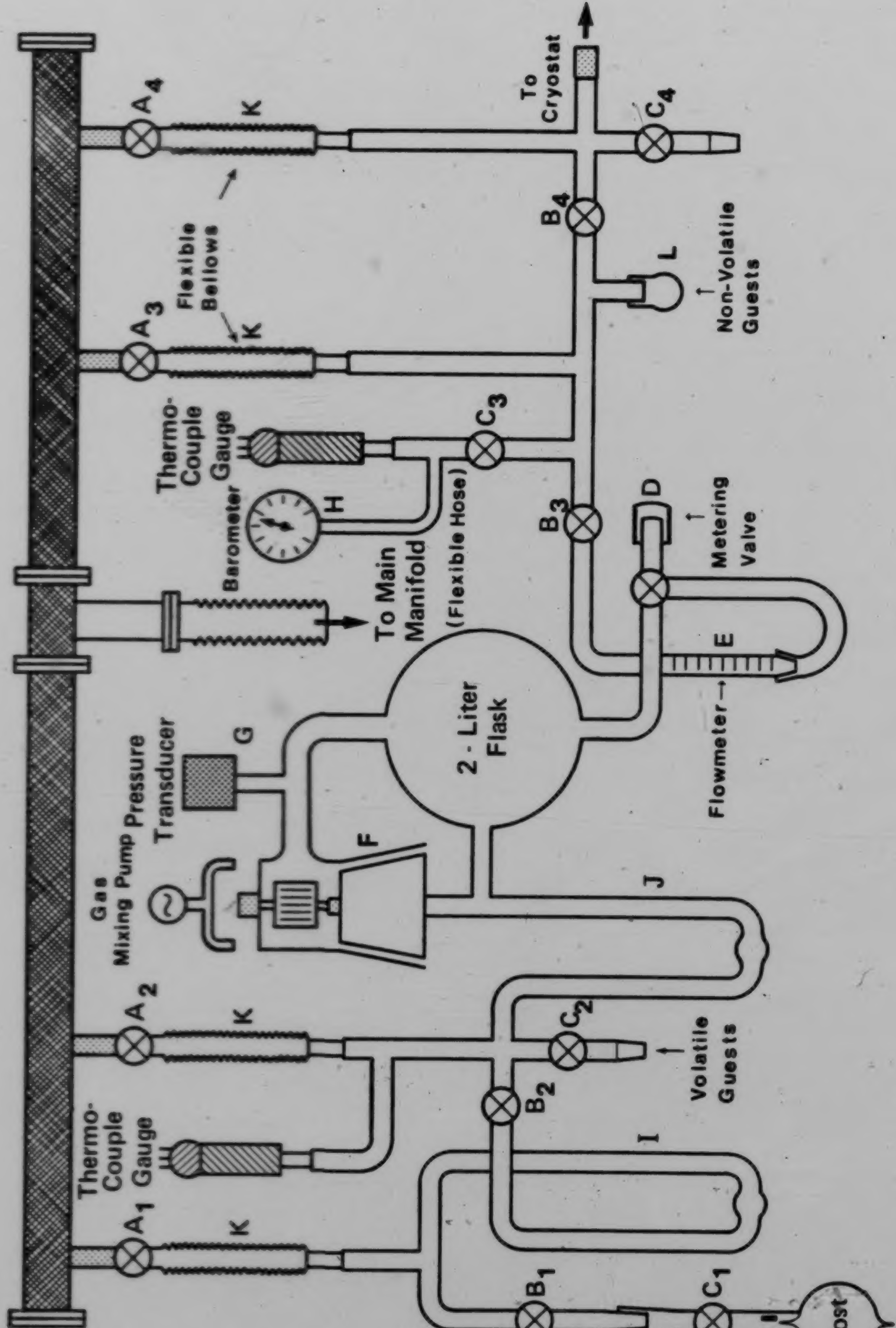
Gas Line for Sample Preparation and Spray-on

The use of gaseous materials as matrices for low temperature work requires external gas-handling apparatus in addition to the cryostat and high vacuum pumping system. The gas line sketched in Figure 29 was designed and built with the highly skilled technical help of the Machine and Glass Shops in this Department. The primary (A_1-A_4) and secondary (B_1-B_4) high vacuum valves used in the assembly were Hoke valves (Zero Leakage Bellows Valves, 4300 Series 316SS and 4200 Series 316SS respectively, Figure 30). Nupro SS-4H bellows valves were used as auxiliary valves (C_1-C_4).

It is convenient to mix the material to be isolated (precursor) with the matrix gas before condensation of the mixture on the cold target (deposition). The rate of the mixing of the matrix gas and precursor depends on the gases involved. Diffusion through heavy gases (like xenon) is particularly slow and adequate mixing requires either a long time or a very turbulent gas flow. Therefore, it is usually more satisfactory to allow the matrix gas and stable precursor to mix in a large spherical bulb than simply to inject one gas into a stream of the other. In the work being described here the matrix gas and volatile precursor were mixed in a 2-liter round bottomed flask using the mixing pump F. The matrix gas (argon or xenon) was led into the

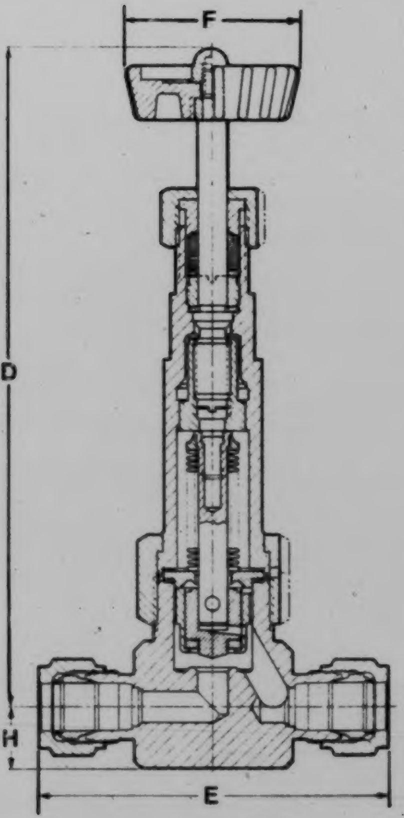
FIGURE 29. Gas Line for Sample Preparation and Spray-On.

A_1-A_4: Primary High Vacuum Valves (Hoke 4300 Series 316-SS, 0.312 Orifice)
B_1-B_4: Secondary High Vacuum Valves (Hoke 4200 Series 316-SS, 0.156 Orifice)
C_1-C_4: Auxiliary Valves (Nupro SS-4H, Bellows Sealed)
D: Micrometering Shut-Off Valve (Whitey 22RS4, Cv = 5×10^{-4}, 1/2 Turn)
E: Flowmeter
F: Gas Mixing Pump
G: Pressure Transducer (Validyne AP-10)
H: Barometrically Compensated Manometer (Edward's, 0-20 Torr)
I: Cold Trap for Host Purification
J: Cold Trap Where Volatile Guests are Transferred
K: Flexible Bellows (Cajon, Glass-Stainless Steel)
L: Finger for Evaporation of Non-Volatile Guests


Thermo-Couple Gauge
A1
K
Thermo-Couple Gauge
A2
K
B1
C1
Host
I
B2
C2
Volatile Guests
Gas Mixing Pump
F
J
Pressure Transducer
G
2 - Liter Flask
To Main Manifold
(Flexible Hose)
Barometer
H
Thermo-Couple Gauge
C3
B3
D
Metering Valve
E
Flowmeter
A3
Flexible Bellows
K
L
Non-Volatile Guests
B4
A4
Flexible Bellows
K
C4
To Cryostat

HOKE 4300 SERIES 316 SS

bellows sealed valves
(.312 orifice)



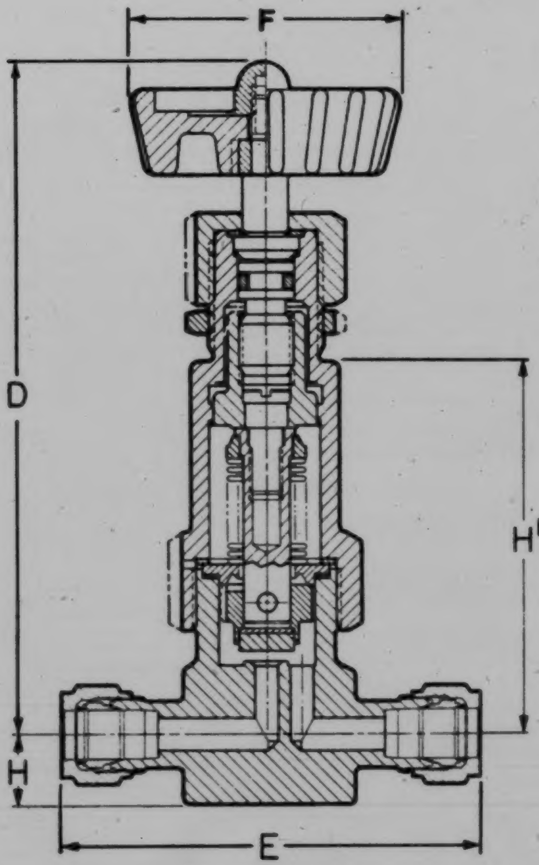
4351G8Y

DIMENSIONS:

		D	E	F	H
4351G8Y	mm	174	90	21	16

HOKE 4200 SERIES 316 SS

bellows sealed valves
(.156 orifice)



4251G4Y

DIMENSIONS:

							Panel Mounting	
		D	E	F	H	H^1	Hole Size	Panel Thick.
4251G4Y	mm	117	55	46	12	64	20	5

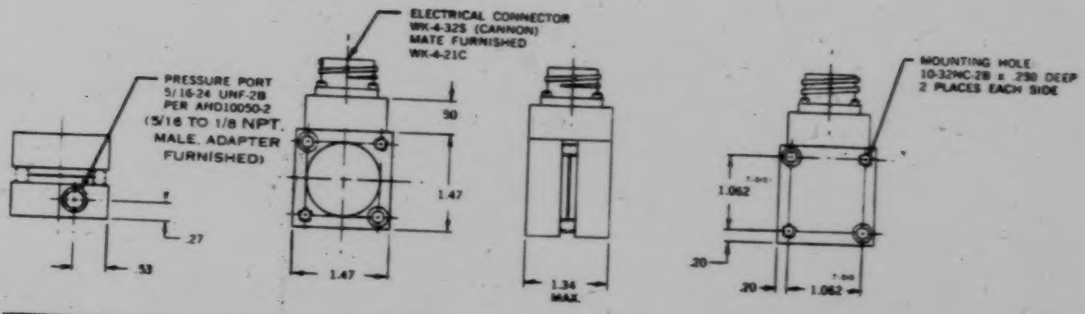
2 Mounting Holes 10-32 NF
Thd., .187 Min. Full Thd.

FIGURE 30. Hoke Bellows Sealed Valves.

flask through the liquid nitrogen (argon) or dry ice-acetone (xenon) trap I (Figure 29). Volatile precursors, having a vapor pressure greater than 250 mTorr at room temperature, were transferred under vacuum to cold trap J and hence to the mixing flask. When mixing was complete, the gas was allowed to flow into the spray-on gas line. The rate of deposition of the matrix gas was dependent upon the pressure in this line. The desired pressure was maintained by regulating the gas flow from the gas-mixing bulb with a Whitey 22RS4 micrometering shut-off valve, D in Figure 29, (Cv = 5×10^{-4}, 1/2 turn). It was monitored by both a thermocouple vacuum gauge (0-1000 mTorr) and an Edward's Compensated Barometer, H (0-20 Torr). The gas flow was measured by observing the small decrease in pressure in the gas reservoir (2-liter flask) during deposition. The pressure drop was monitored with a Validyne[106] DM56A Digital Manometer (AP-10 Absolute Pressure Transducer, G in Figure 29, and CD23 Digital Transducer Indicator, Figure 31). The pressure transducer and Edward's barometer have been of invaluable help in the control of the entire deposition process and so in the achievement of reproducible experimental conditions.

Precursors whose vapor pressure was less than 100 mTorr at room temperature were not introduced into the missing bulb but were placed in the finger L and warmed

AP10 Absolute Pressure Transducer


ELECTRICAL CONNECTOR
WK-4-32S (CANNON)
MATE FURNISHED
WK-4-21C
PRESSURE PORT
5/16-24 UNF-2B
PER AND10050-2
(5/16 TO 1/8 NPT.
MALE. ADAPTER
FURNISHED)
.90
1.47
.27
.53
1.47
1.34
MAX.
MOUNTING HOLE:
10-32NC-2B x .230 DEEP
2 PLACES EACH SIDE
1.062
.20
.20
1.062

CD23 Digital Transducer Indicator

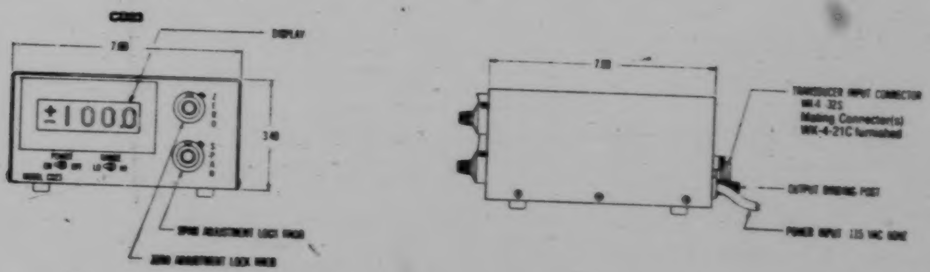

DISPLAY
±1000
ZERO
SPAN
3.40
ZERO ADJUSTMENT LOCK KNOB
TRANSDUCER INPUT CONNECTOR
WK-4-32S
Mating Connector(s)
WK-4-21C furnished
OUTPUT BINDING POST

FIGURE 31. Validyne DM56A Digital Manometer.

in a bath of hot liquid until the vapor pressure was between 10 and 100 mTorr. Where a bath temperature greater than 60-70°C was required, the entire spray-on line was warmed (80-100°C) by wrapping the tubes with resistance heated nichrome tape to prevent condensation of the precursor. The sample vapor effusing from the finger was led into the stream of matrix gas from the metering valve D and the resultant mixture was condensed on the cold target to form the matrix.

Connection of the Cryostat and Gas Line to the Main High Vacuum Manifold

When operating a system at pressures of less than about 10^{-4} Torr, the ultimate pressure attainable and the speed at which it can be reached are highly dependent on the geometry of the system.[105] Any constriction or bend markedly reduces the effective pumping speed at pressures below about 10^{-5} Torr where "molecular flow" occurs (most molecules will need to make at least one wall-collision to pass the obstruction). Therefore, the system designed for the current study was arranged so that as far as possible the low pressure gases moved along straight line paths. However, since the vacuum port of the cryostat (Displex microrefrigerator) protrudes at right angles to the vertically mounted vacuum shroud, one 90° angle in the connection between the cryostat and the pump was unavoidable. The entire evacuation tubes connecting both the gas line and the cryostat to the pump were also kept as short and as wide as practical. All couplings or flexible sections were contructed so that they would not act as constrictions. The cryostat and gas line were connected to the main vacuum manifold through Varian "Stainless Steel Roughing Hoses". These were two 18-inch long, 1 1/2-inch OD hoses made of thin-walled bellows covered with flexible braid for extra strength and protection. All high vacuum permanent connections were made through 2 3/4-inch OD ConFlat® Flanges and oxygen-free-high-conductivity copper gaskets. Varian Stainless Steel Fittings were used where required (Figures 29 and 32). The flexible hose E from the pump to the cryostat was equipped with a roughing valve (F) mounted on a two-sided ConFlat® flange. This roughing valve was connected through a Varian Molecular Sieves Trap (Figure 33) to an auxiliary 2.5 CFM mechanical pump. This connection was made with a short piece of latex high vacuum tubing. The cryostat itself (A) was equipped with a Nupro Bellows-Sealed Butterfly Valve BV_1) and a cold cathode vacuum gauge C (NRC 524-2 Gauge with Flange) connected to a Varian "T" fitting (D), as illustrated. The purpose of the cold head vacuum gauge was to monitor at all times the pressure in the system as close as possible to the cryostat. Finally, the

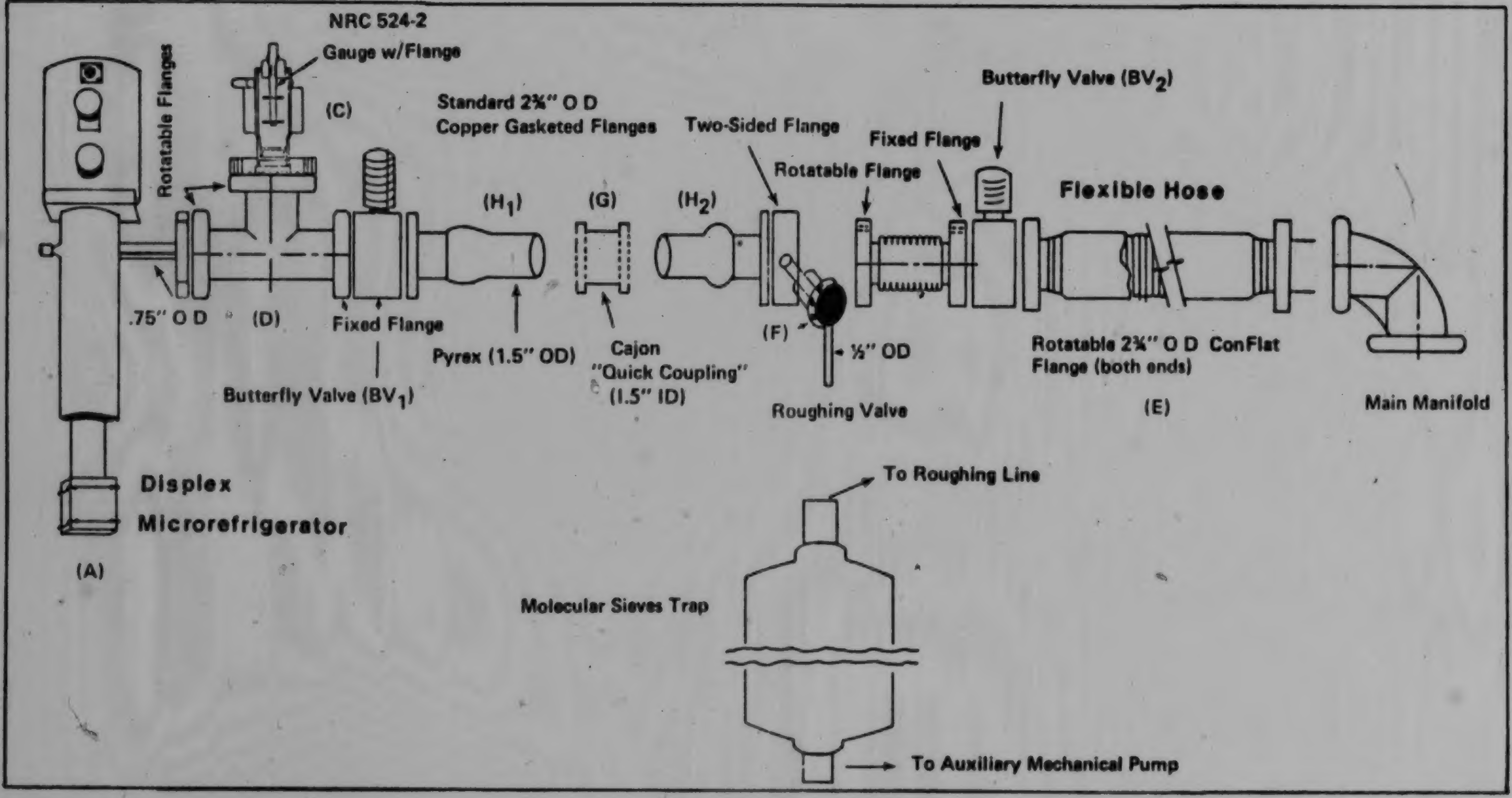

NRC 524-2
Gauge w/Flange
(C)
Rotatable Flanges
.75" O D
(D)
Fixed Flange
Butterfly Valve (BV$_1$)
Standard 2¾" O D
Copper Gasketed Flanges
(H$_1$)
Pyrex (1.5" OD)
(G)
Cajon
"Quick Coupling"
(1.5" ID)
(H$_2$)
Two-Sided Flange
Rotatable Flange
(F)
½" OD
Roughing Valve
Fixed Flange
Butterfly Valve (BV$_2$)
Flexible Hose
Rotatable 2¾" O D ConFlat
Flange (both ends)
(E)
Main Manifold
Displex
Microrefrigerator
(A)
To Roughing Line
Molecular Sieves Trap
To Auxiliary Mechanical Pump

FIGURE 32. Evacuation Tube Connecting the Cryostat (Displex Microrefrigerator) to the Main High Vacuum Manifold.

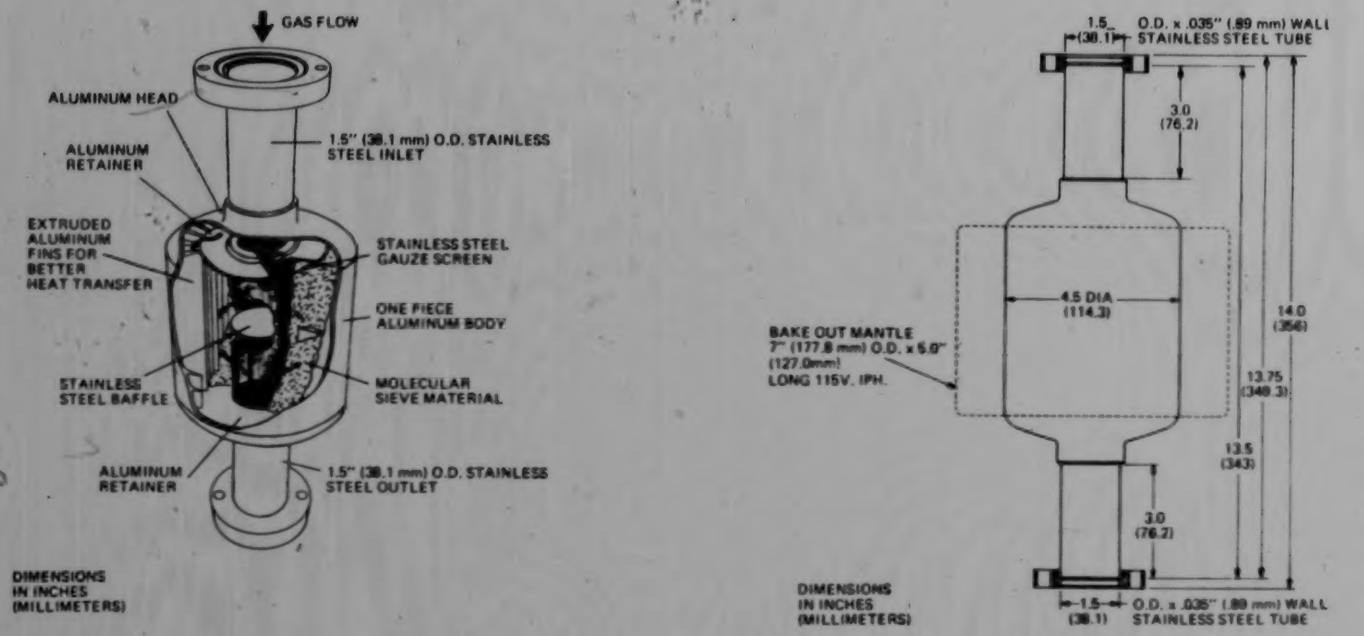

GAS FLOW
ALUMINUM HEAD
1.5" (38.1 mm) O.D. STAINLESS STEEL INLET
ALUMINUM RETAINER
EXTRUDED ALUMINUM FINS FOR BETTER HEAT TRANSFER
STAINLESS STEEL GAUZE SCREEN
ONE PIECE ALUMINUM BODY
STAINLESS STEEL BAFFLE
MOLECULAR SIEVE MATERIAL
ALUMINUM RETAINER
1.5" (38.1 mm) O.D. STAINLESS STEEL OUTLET
DIMENSIONS IN INCHES (MILLIMETERS)
1.5 (38.1)
O.D. x .035" (.89 mm) WALL STAINLESS STEEL TUBE
3.0 (76.2)
4.5 DIA (114.3)
BAKE OUT MANTLE 7" (177.8 mm) O.D. x 5.0" (127.0mm) LONG 115V. 1PH.
14.0 (356)
13.75 (349.3)
13.5 (343)
3.0 (76.2)
DIMENSIONS IN INCHES (MILLIMETERS)
1.5 (38.1)
O.D. x .035" (.89 mm) WALL STAINLESS STEEL TUBE

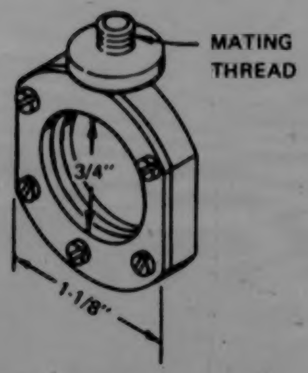
FIGURE 33. Varian Molecular Sieves Trap.

connection of the cryostat to the flexible coupling line was achieved with a Cajon Ultra-Torr Coupling Union, G (1.5" OD) through glass on ConFlat ® flanges (H_1 and H_2).

The use of only stainless steel and pyrex and the permanent vacuum connections described above, provided a system with a very low rate of outgassing making pressures of the order of 2×10^{-6} to 5×10^{-7} Torr readily accessible.

Cold End and Vacuum Shroud

The target on which the matrix gas mixture was condensed consisted of a highly polished CsI plate (25 mm OD x 3 mm) mounted in a DMX-1 nickel-plated copper optical sample holder supplied by Air Products.[102a] This target was affixed (mating thread) to the tip of



DMX-1 Optical Sample Holder

the cold end of the Displex microrefrigerator. Thermal contact between the cold tip and the CsI plate was maintained with indium gaskets (Figure 34). A standard Air Products radiation shield was mounted on the first expansion stage (44°K) of the Displex cold end, and thermal contact between them was ensured by using Cryo-Con® grease. After being installed, the radiation shield had to be unscrewed by no more than half a turn in order to align it with the CsI target window.

The cold end was surrounded by a DMX-1 general purpose vacuum shroud also supplied by Air Products (Figure 34). This square-shaped shroud was fitted with highly polished CsI windows (33 mm OD x 6 mm) on two opposite sides and on the remaining sides with Spectrosil quartz windows (33 mm OD x 3 mm), all mounted on Viton "O"-rings (Figures 34 and 35a).*

The matrices were deposited onto the cold target plate by spraying the sample beam from the gas line (Figure 29, p. 168) through a short piece of 1/16" OD soft stainless steel tube (deposition needle) inserted into

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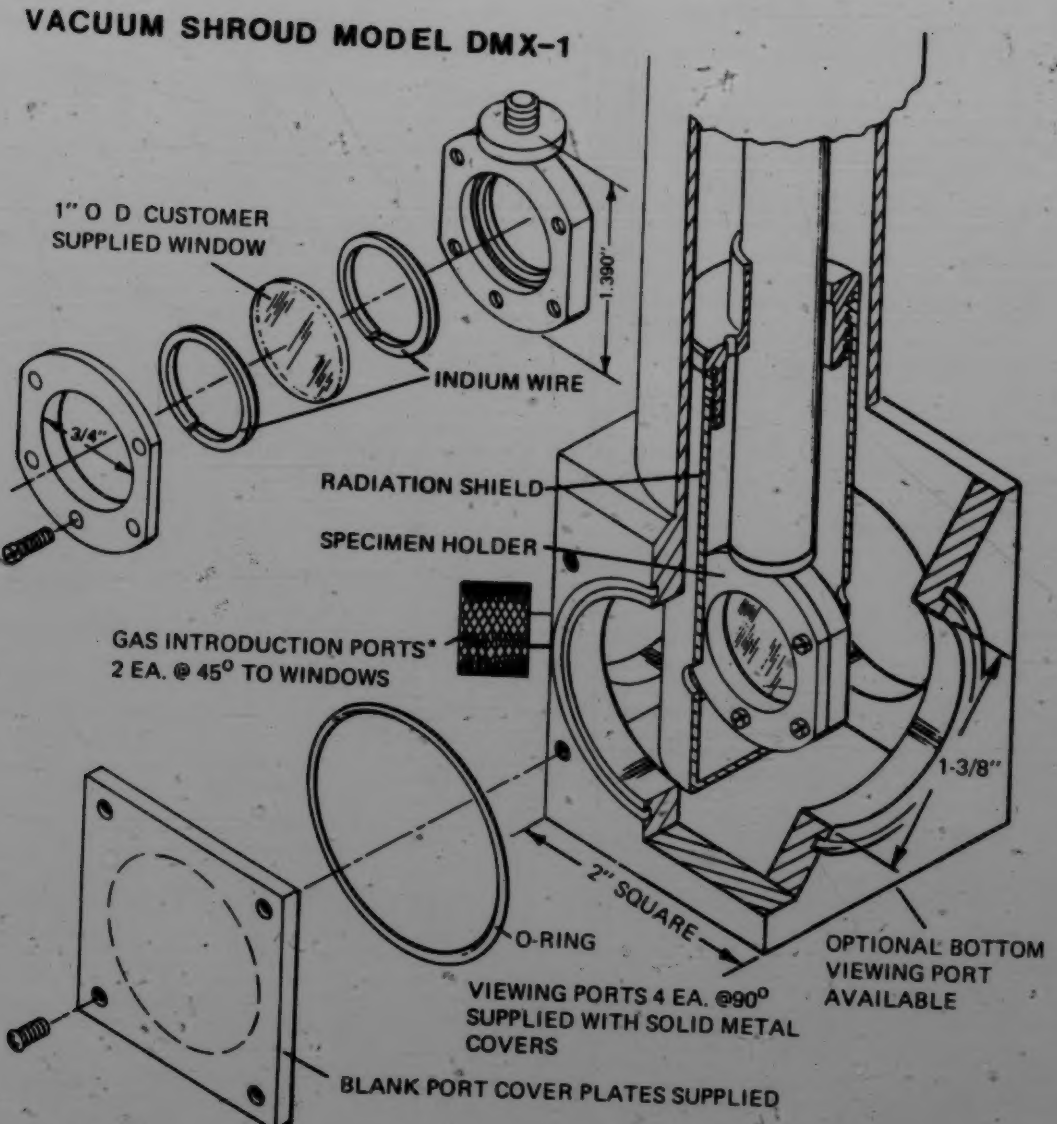
* The window mounts were made in the Machine Shop of this Department. The Glass Shop supplied the Spectrosil quartz plates and the CsI plates were purchased from International Crystal Laboratories, Elizabeth, New Jersey 07206.


VACUUM SHROUD MODEL DMX-1
1" O D CUSTOMER SUPPLIED WINDOW
1.390"
INDIUM WIRE
3/4"
RADIATION SHIELD
SPECIMEN HOLDER
GAS INTRODUCTION PORTS* 2 EA. @ 45° TO WINDOWS
1-3/8"
2" SQUARE
O-RING
OPTIONAL BOTTOM VIEWING PORT AVAILABLE
VIEWING PORTS 4 EA. @90° SUPPLIED WITH SOLID METAL COVERS
BLANK PORT COVER PLATES SUPPLIED

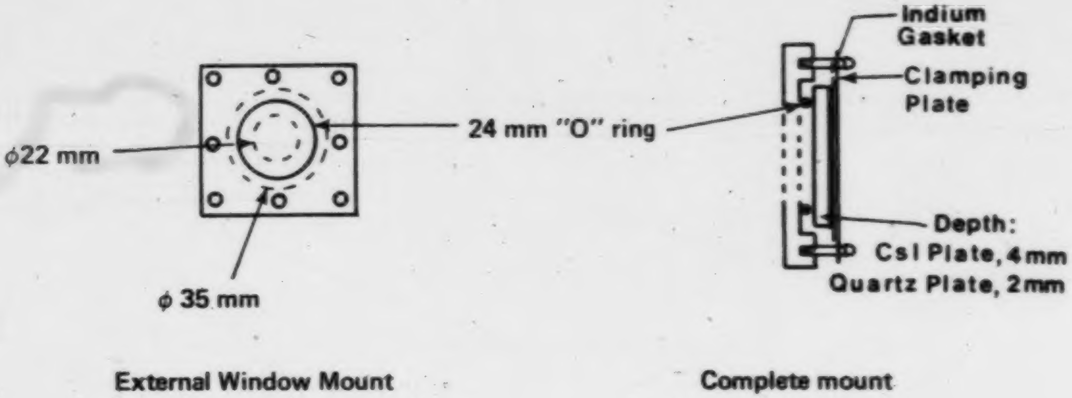
This vacuum shroud provides, in addition to the four standard windows, two 1/16-inch diameter vacuum quick-connect fittings* at 45° to the windows. These fittings allow the direct introduction of gaseous samples for deposition onto the cold surface at the end of the refrigerator.

FIGURE 34. Air Products DMX-1 Vacuum Shroud for Optical Spectroscopy.

one of the gas introduction ports of the vacuum shroud (Figure 34). The deposition needle was isolated from the atmosphere or from the spray-on gas line by means of a Nupro SS-2H bellows-sealed, shut-off valve (Figure 35b). This valve was vertically mounted on a holder through the two threaded holes at the base. The holder was then clamped onto the lower end of the vacuum shroud, just above the optical windows.

The Displex vacuum shroud fitted as described above could be rotated while maintaining the vacuum in the cryostat. The optical windows were kept in an atmosphere of argon when the cryostat was not in service. A demountable transparent plastic box was used for this purpose.

The connection between the spray-on gas line and the cryostat deposition shut-off valve was made with two 1/4-inch OD Cajon flexible-bellows stainless steel and glass tubes with the appropriate quick-coupling fittings.


Indium
Gasket
Clamping
Plate
24 mm "O" ring
ϕ22 mm
ϕ 35 mm
Depth:
CsI Plate, 4 mm
Quartz Plate, 2 mm
External Window Mount
Complete mount

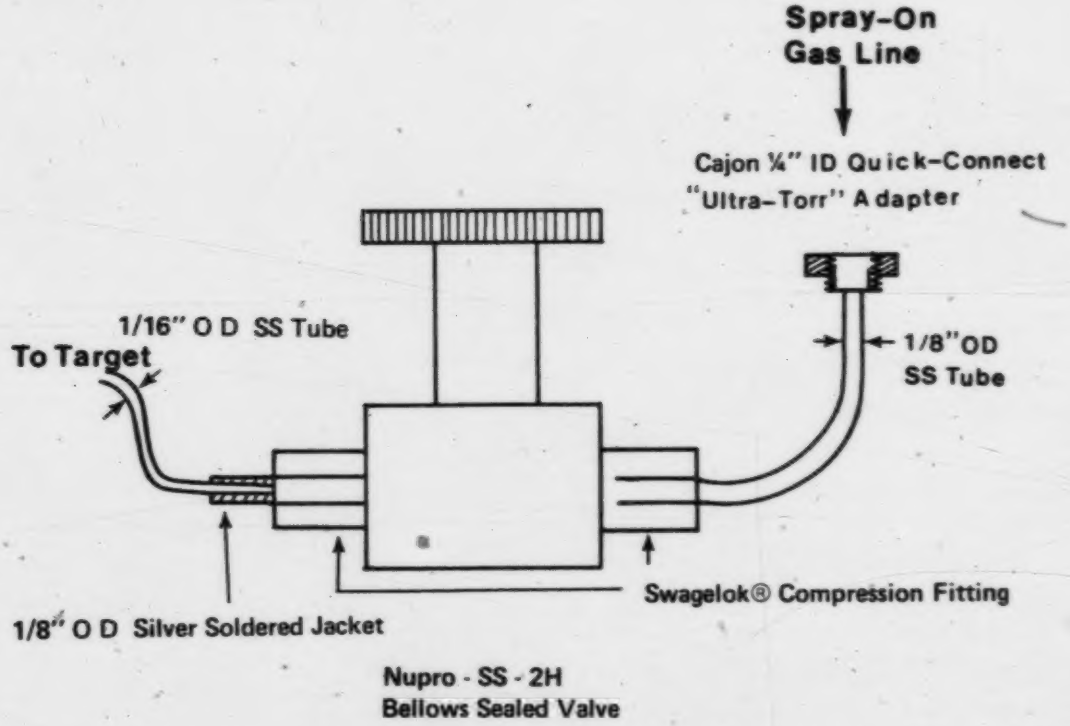

Spray-On
Gas Line
Cajon ¼" ID Quick-Connect
"Ultra-Torr" Adapter
1/16" O D SS Tube
To Target
1/8"OD
SS Tube
Swagelok® Compression Fitting
1/8" O D Silver Soldered Jacket
Nupro - SS - 2H
Bellows Sealed Valve

FIGURE 35. a) External Window Mounts.

b) Deposition Needle Shut-off Valve.

FORMATION OF MATRICES

Cooling of the Target and Preparation of the Matrix-Precursor Mixture

In preparation for the deposition of a matrix, the Displex sample chamber and the spray-on gas line were evacuated for ~18 h at room temperature with the main cryotrap filled with liquid nitrogen. Pressures of 2×10^{-6} to 5×10^{-7} Torr (measured with the cold cathode vacuum gauge) were achieved so that residual gases were removed. The Displex compression unit was started with the digital micro-voltmeter temperature read-out and automatic temperature controller in service, and the target was thereby cooled to the desired temperature. A temperature of 77°K was reached in 45-60 min, of 10°K in 75-90 min, and of 7-8°K in ~120 min.

During this cooling period, trap I (Figure 29, p. 168) of the gas line was also cooled with liquid nitrogen (for Ar) or dry ice-acetone (for Xe) and then the gas line was isolated from the main vacuum manifold (valves A_1-A_4, B_3, and D closed; valves B_1 and B_2 open) and from the cryostat (shut-off valve of the deposition needle closed). The samples of precursors which were volatile at or below room temperature (vapor pressure >250 mTorr, 25°C) were degassed (p. 205) and vacuum transferred to trap J through valve C_2 (valve B_2 closed).

Trap J contained liquid nitrogen to keep the sample frozen. With valves C_1, B_1 and B_2 open and B_3 and D closed, argon or xenon was introduced through trap I into the mixing bulb (2-liter flask in Figure 29) to a pressure of 40 to 70 Torr.* The bulb was isolated from the rest of the system by closing valve B_2, the liquid nitrogen bath was removed from trap J and the vaporized sample and noble gas were stirred with the mixing pump F for 30-45 min. The resulting pressure was recorded and used as the starting value of the pressure of the reservoir.

---

* The choice of ratio of precursor to noble gas was governed by the following factors. A highly diluted mixture (1:1000 or 10,000) is desirable to ensure suppression of dimerization of the photoproduct, cyclobutadiene. However, in order to observe weak absorptions in the spectrum, it would then be necessary to deposit a thick matrix. Such matrices tend to crystallize and usually scatter the photolytic radiation to an unacceptable extent (this is particularly severe in the case of Xe at 4.2°K). Matrix to guest ratios of 100 to 500 are common in the preparation of chemically unstable species in situ by photolysis of a precursor and they have been found to be suitable for the presently described work.

In the case of precursors which were non-volatile at room temperature (vapor pressure <100 mTorr at 25°C), the sample was introduced and degassed (p. 205) through the "finger" L. The sample vapor (vapor pressure of 10-100 mTorr measured with the thermocouple gauge) effusing from the finger warmed to the appropriate temperature (p. 173) was in this cases mixed during deposition with the stream of matrix gas flowing from the metering valve D.

When the target had reached temperatures of 20°K or below, all valves connecting the cryostat to the other parts of the system were closed. The cryopumping action of cold surfaces at 4.2 or 20°K is more efficient than a liquid nitrogen trap or diffusion pump, therefore it is better to operate a static vacuum system once those temperatures have been reached.

To ensure that there had not been any serious contamination of the CsI target plate during the cooling process described above, a "blank" infrared spectrum was always run before deposition was attempted.

Deposition of the Matrix-Precursor Mixture

The spray-on vacuum line (Figure 29) was connected to the shut-off valve of the deposition needle (Figure 35b). The volume between valve B_3 and the shut-off valve was evacuated (valves A_3, A_4 and B_4 open) and then isolated (valves A_3 and A_4 closed and valve B_3 open). The flow of gases from the mixing bulb was regulated with the micrometering valve (D) until a reading of 2.0 to 2.5 SCC/min was observed in the flowmeter E. The shut-off valve of the deposition needle was opened to allow passage of the sample beam when a pressure of 2.5 to 3.0 Torr (measured with the Edward's barometer H) was reached in the spray-on gas line. For non-volatile precursors, before the sample vapor was allowed to effuse, a 2.5-3.0 Torr pressure of matrix gas was reached in the line. The "finger" containing the sample was then warmed to the desired temperature (vapor pressure of 10-100 mTorr) and the shut-off valve was opened (this provided a homogeneous gas beam). The beam was thereby fed into the cryostat through the deposition needle. Some of it condensed on the cold target to form the matrix and any that escaped immediate condensation was removed by the "cryopumping" action of other cold parts of the apparatus. The rate at which the gas was introduced was carefully controlled with the micrometering valve.*

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* If excessive pressure rise is allowed to occur, heat transfer across the cryostat may become too great and the experiment might be aborted (vide infra).

70

The deposition needle was positioned at right angles to the target by rotation of the vacuum shroud and was then barely inserted into the opening of the radiation shield (the tip of the needle was held at approximately 3 cm from the CsI target plate). The needles used had orifices between 0.8 and 1.0 mm in diameter. This arrangement produced a gas beam that was uniform over the 20-mm width of the CsI target plate and allowed to pass 1-2 mmol (4-7 Torr) of gas at room temperature per hour when the pressure in the spray-on gas line was of 2.5 to 3.5 Torr.

Optimization of the Cold Target Temperature

The density and structure of matrices depends on the temperature gradient, deposition speed, heat of sublimation of the matrices, and many other factors (Table 7). Slow deposition rates caused amorphous solids with crystals imperfections.* This gave rise to heavy light scattering reducing enormously the observed quantum yield of the sample. The resulting spectra were usually broad and ill defined. Exceptionally high

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* At slow deposition speeds and very cold temperatures (4.2-10°K) both the guest and the host are trapped at or near the point of contact with the cooled surface. This causes crystals imperfections, lattice vacancies and "snow".

Substance	Temperature (°K)							Atomic Weight
	Melting Point	Boiling Point	10^{-7} Torr	10^{-5} Torr	10^{-3} Torr	10^{-1} Torr	10 Torr	
Rare Gases								
He	-	4.216	-	0.486	0.658	0.980	1.738	4.003
Ne	24.57	27.1	7.87	9.19	11.05	13.85	18.45	20.18
Ar	83.85	87.29	28.6	33.1	39.2	48.2	62.5	39.944
Kr	115.95	119.93	39.3	45.5	53.9	66.3	85.9	83.80
Xe	161.3	165.1	54.2	62.7	74.4	91.5	118.5	131.30
Rn	202	211.3			96.9	137.5	160.0	222.00

TABLE 7. Physical Properties of Matrix Materials.[93]

flow rates, on the other hand, led to considerable warming of the surface of the growing matrix and this resulted in an excessive pressure rise in the cryostat (> 5×10^{-4} Torr).

The collection efficiency is also a factor to be considered. It is expressed as the "sticking probability" of the molecules to be condensed (the proportion of molecules striking the cold surface that actually condense). Since the "sticking coefficient" of most condensable materials approaches unity at around 20°K, the temperature of the cold tip of the Displex microrefrigerator used in this research was optimized between ca. 7 and 20°K. Temperatures between 16 and 18°K have been found to give clear, glass-like argon matrices with a gas flow rate of 4-7 Torr (1-2 mmol) per hour and a static vacuum in the cryostat of 5×10^{-4} to 5×10^{-5} Torr.

The matrix gas has a poorer thermal conductivity than the CsI plate or the copper sample holder so that, as the thickness of the matrix increases, the condensation of the incoming gas beam becomes less efficient and a gradual loss of vacuum occurs in the isolated cryostat. Under these conditions the pressure in the cryostat is a function of both the flow rate of the gases being introduced and the temperature of the cold target. Since it is more convenient to operate with a constant flow of matrix materials, this increase in

Thermal Conductivity of Rare Gases[a]

Rare Gas	Thermal Conductivity[b]			Maximum λ	
	4.2°K	20.4°K	77°K	Value λ	T (°K)
Neon	41	37	-	47	3.4
Argon	17	12	3.4	38	8.2
Krypton	5.2	11	3.5	17	11.5
Xenon	-	-	-	24	16.1

[a] Data from G.K. White (1956) and Pollack (1964).[93]

[b] λ in mW/cm·degree Kelvin.

pressure in the cryostat during deposition was controlled by stepwise lowering of the temperature of the target (temperature controller) in such a way as to maintain a pressure of 5×10^{-4} to 5×10^{-5} Torr.

The deposition process was monitored and controlled by closely observing the values of the following parameters.

Time	Reservoir Pressure (Torr)	Flow Rate (SCC/min, flow meter)	Line Pressure (Torr)	Cold Tip Temperature		Cryostat Pressure (Torr)
				Controller (Ω)	Readout (°K)	

To achieve reproducible experimental conditions a close record of these values at 10-15 min intervals was kept.

No more than 1-2 mg of precursor were deposited in any one experiment. When the deposition was finished (1-3 hours), the temperature of the target was gradually lowered to the minimum value (ca. 7-8°K) before photolysis was begun. An infrared spectrum of the starting material was taken during this cooling process.

PHOTOLYSIS OF THE MATRIX-ISOLATED PRECURSORS

Cyclobutadiene was generated by photolysis of the matrix-isolated precursors. The matrices were irradiated as indicated in Figure 36. The progress of the photolysis was monitored spectroscopically at different time intervals. Since the quartz windows on the Displex vacuum shroud were arranged at right angles to the spectroscopic windows, the vacuum shroud was rotated through 90° for photolysis and then back again before the progress of the irradiation could be monitored. If necessary, the photolytic process was completed by irradiation from both sides of the matrix with two identical lamps of the desired wavelength (medium or low pressure mercury vapor lamps). Some warming of the cold tip was usually observed during this process but the temperature did not rise above about 10°K.

Using a set of filters (Table 8) in conjunction with the Quartz cryostat windows, radiation bands of different energies were selected for each precursor to optimize the yield of cyclobutadiene while minimizing the formation of side products. The energy distribution for the Hanovia medium pressure mercury vapor lamp (140 W) which was used for the photolysis is given in Table 9.

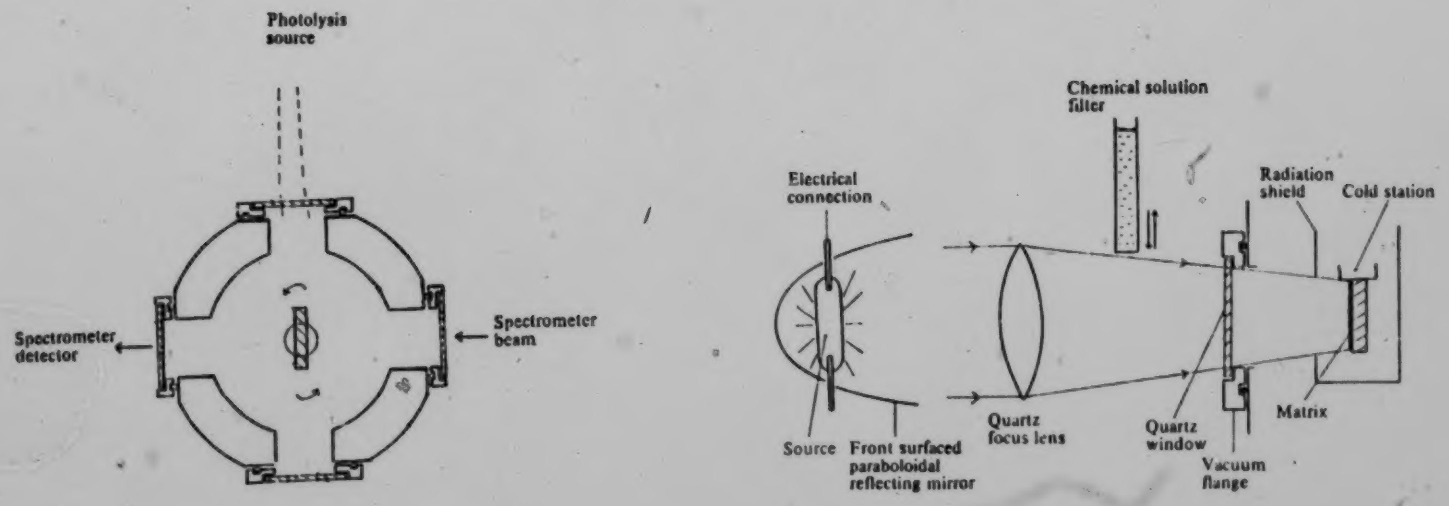

Photolysis source
Spectrometer detector
Spectrometer beam
Chemical solution filter
Electrical connection
Radiation shield
Cold station
Source
Front surfaced paraboloidal reflecting mirror
Quartz focus lens
Quartz window
Vacuum flange
Matrix

FIGURE 36. Illumination Geometry for Photolysis.[44]

Filter Type	High-Energy Cut-off (nm)
Vycor (7910)	220
Corex (97100)[a]	270 (~220)[a]
Pyrex (7740)	290
Uranium glass	330

[a] Maleski and Morrison[107] report a change in the properties of Corex.

TABLE 8. Filters for Hanovia Mercury Lamps.

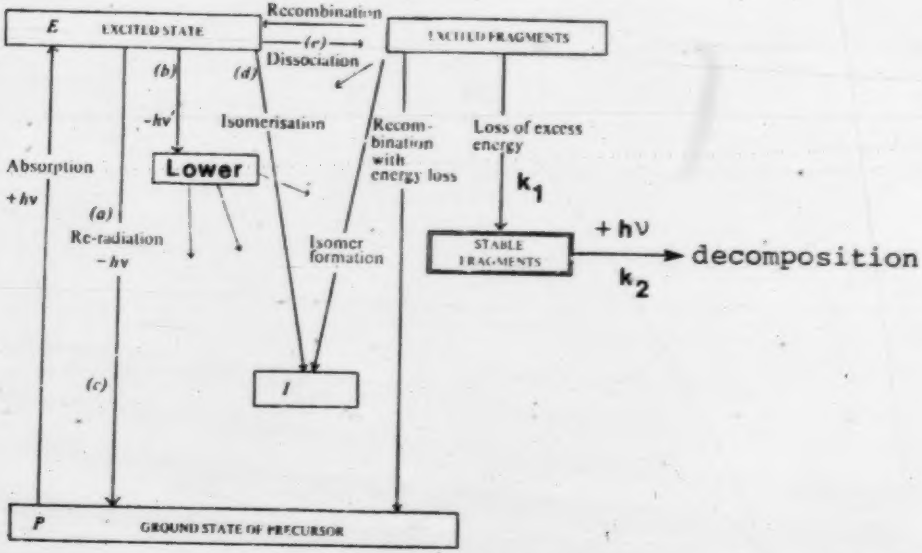
Wavelength (Å)	Energy (W)	Wavelength (Å)	Energy (W)
Ultraviolet		Visible	
1847 (reversed)	1.5	4045	3.4 violet
2482	0.7	4358	6.3 blue
2537 (reversed)	1.8	5461	7.6 green
2652	1.2	5780	6.2 green
2804	0.7	Infrared	
2967	1.3	10140	3.3
3025	2.2	11287	1.0
3130	4.1	13673	0.8
3341	0.7		
3360	8.0		

(The Southern New England Ultraviolet Co.)

TABLE 9. Energy Distribution for the 140-W Hanovia Medium Pressure Mercury Lamp.

Results of Photolysis

Irradiation of a solid within a matrix poses many problems. Absorption of the incident ultraviolet light by the matrix raises the substrate molecules contained within (P) to a electronically excited state (E). The excited state may either re-radiate the absorbed energy (a or b), lose energy without radiating (c) or dissociate into several fragments (e). Dissociation leads to formation of the desired compound but the initially formed fragments are essentially in contact, trapped in the cage occupied by the precursor and one or more fragments will be excited. Recombination of these reactive fragments can be avoided only if one


E
EXCITED STATE
Recombination
(e)
Dissociation
EXCITED FRAGMENTS
(b)
(d)
-hν'
Isomerisation
Recombination with energy loss
Loss of excess energy
Absorption
+hν
Lower
k1
(a)
Re-radiation
-hν
Isomer formation
+ hν
STABLE FRAGMENTS
decomposition
k2
(c)
I
P
GROUND STATE OF PRECURSOR

(From reference 44)

of them is an inert molecule[*] and/or the excitation energy can be removed rapidly from the system. The excess energy can be lost by dissipation through the matrix to the cooling block. It is usually transmitted across the matrix in the form of "lattice vibrations" which are low energy processes, and therefore considerable local warming may result.

The Effects of Continued Photolysis

Prolonged irradiation might be expected to result in complete conversion of the precursor to products, even if most individual precursor molecules have to be excited many times before forming the desired product. This situation is precluded by (i) the formation of by-products, (ii) the absorption of the exciting radiation by the desired product leading to its decomposition, and (iii) scattering of the photolytic radiation by the matrix. No build-up of the desired product will be seen if the probability of decomposition is equal to or exceeds the probability of formation ($K_2 \geqslant K_1$, see above diagram). Under certain circumstances, ($K_1 > K_2$) a "steady state" concentration of product will be formed. If it is possible to find a wavelength of light absorbed by the precursor but not by the product (selective photolysis), then an almost complete photoconversion may result.

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[*] In some cases, even molecular nitrogen is not unreactive enough to survive in close proximity to the excited fragment.[108]

SPECTROSCOPIC METHOD AND SPECTROPHOTOMETER

The infrared spectra of the photolysates of all matrix-isolated precursors were initially recorded with a Perkin-Elmer 457 Grating Infrared Spectrophotometer equipped with ordinate expansion facility. These exploratory experiments proved rather disappointing yielding inconsistent results. This was at least partly due to the low concentration of cyclobutadiene which could be formed within the matrix. The concentration was limited by two factors, incomplete photolysis of precursor isolated in thick matrices ("scattering" of photolytic radiation), and destruction of the molecules already generated by photocleavage to acetylene. Since there were weak features in the spectrum which it was necessary to detect and identify, the use of a dispersive instrument with improved performance standards was warranted. Therefore, a series of infrared spectra of the photolysates of all precursors were recorded, plotted and stored using a Nicolet 7199 FT-IR Spectrophotometer and the desired features were successfully observed. The Nicolet Spectrophotometer was also of invaluable help in determining with accuracy the integrated absorptions of the bands assigned to cyclobutadiene. The integrated intensity (cm^{-1}), $I = \int A(w)dw$, was estimated by assuming a Gaussian band contour and then relating the integrated intensity to the absorbance at the absorption maximum (A_{max}), and the half-width ($\Delta_{w1/2}$).[109]

$$\int A(w)dw \;\alpha\; A_{max} \cdot \Delta_{w1/2}$$

This allowed the computation of the relative intensities of the bands (Table 3).

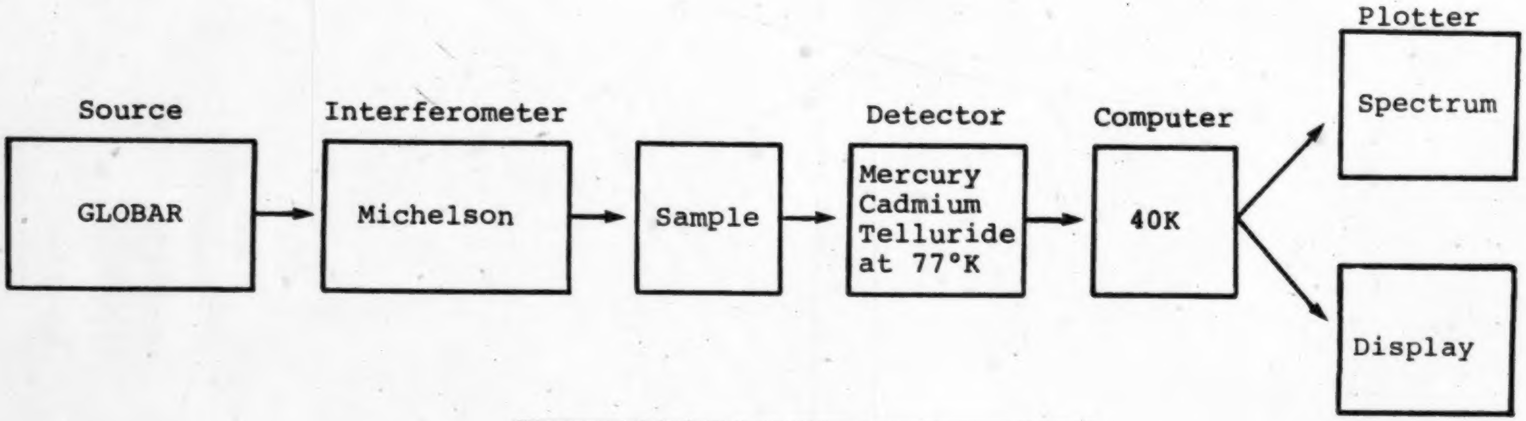
The basic components of the Nicolet 7199 FT-IR Spectrophotometer are schematically represented in Figure 37.

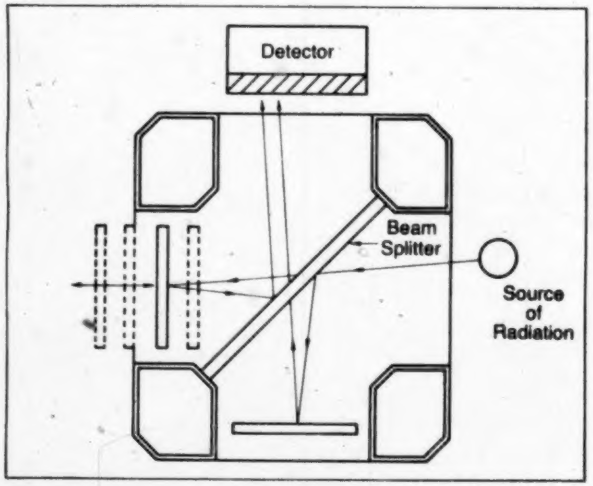
Fourier Transform (Multiplex) Infrared Spectroscopy[111] exceeds the performance standards associated with high quality grating infrared spectrophotometers. The advantages of FT-IR Spectrophotometers are threefold:

1. The detector "sees" the full intensity of the source without an entrance slit. The improvement is roughly a factor of 100.
2. The signal-to-noise ratio is theoretically improved by a factor of $N^{1/2}$ for an interferometer, where N is equal to the number of resolving elements.
3. An adequate signal-to-noise ratio for this

FIGURE 37. Basic Components of the Nicolet 7199 FT-IR Spectrophotometer.

The source is directed into the Michelson interferometer,[110] which consists of two mirrors and a beam splitter. In the interferometer, the intensity of each wavelength component is converted into a modulated (ac) audio frequency waveform. The beam splitter transmits half of all incident radiation to the moving mirror and reflects half to the stationary mirror. One half of the incident radiation is thereby passed through the sample. Each component reflected by the two mirrors returns to the beam splitter where the amplitudes of the waves are combined to form an interferogram as seen by the detector.


Source
GLOBAR
Interferometer
Michelson
Sample
Detector
Mercury Cadmium Telluride at 77°K
Computer
40K
Plotter
Spectrum
Display


Detector
Beam Splitter
Source of Radiation

The Michelson Interferometer

study required approximately 2 min using the Nicolet Interferometer, as against 50 min using the dispersive spectrophotometer. The software and data handling facilities of the Nicolet were also a merit, as well as such features as constant resolution over the range of the instrument, photometric accuracy, automatic calibration, plotting accuracy, computer storage of data and direct plotting for slide preparation. The interferograms (100-500 scans) were computer stored, averaged, and Fourier transformed into the usual frequency spectrum.

"WARM-UP" EXPERIMENTS

Warming the argon matrices to about 35°K caused the cages to lose their rigidity allowing the cyclobutadiene molecules to diffuse and so dimerize. The resultant spectral changes aided the assignment of the absorptions to individual species.

Rigidity of Matrices[93]

Matrix	Matrix Temperature[a]					
	4.2°K	12°K	20°K	40°K	60°K	77°K
Ne	17	49	82	-	-	-
Ar	5	14	24	48	72	92
Kr	4	10	17	34	52	66
Xe	3	7	12	25	37	48

[a] Expressed as percentage of matrix melting point.

Thus, "warm-up" experiments were helpful in the selection and assignment of infrared bands to cyclobutadiene and were carried out as follows. After photolysis was complete or the desired degree of photoconversion had been achieved, the matrix was warmed to a predetermined temperature which was held constant for a period of time. This time and temperature was governed in each case by the reactivity and mobility of cyclobutadiene in the presence of the other trapped species. Warming of the matrix caused the pressure in the static cryostat to rise (vide supra). For this reason "warm-up" experiments were always closely followed and carefully executed. The spectral changes observed were represented by graphical plots of band intensity (integrated absorbance) as a function of temperature and/or time.

Diffusion Controlled Dimerization

The dimerization of cyclobutadiene in the warmed matrix is a diffusion-limited bimolecular reaction. The apparent rate constant for such reactions is time dependent[112] and the following rate equation has been derived.[113]

$$-\frac{d[X]}{dt} = 4\pi r_\circ \left(D_X+D_Y\right)\left(1 + \frac{r_\circ}{(\pi(D_X+D_Y)t)^{1/2}}\right)[X][Y]$$

$[X],[Y]$ = concentration of reagents

D_X, D_Y = diffusion coefficients

$r_\circ$ = X-Y separation below which reaction is ensured.

In the case of a dimerization process,

$$2X \longrightarrow X_2$$

$$-\frac{d[X]}{dt} = 8\pi r_\circ D \left(1 + \frac{r_\circ}{(2\pi Dt)^{1/2}}\right)[X]^2$$

and

$$\frac{[X]}{[X_\circ]} = \frac{1}{A[X_\circ]t + 2ab[X_\circ]t^{1/2} + 1}$$

where $a = 8\pi r_\circ D$ and $b = \frac{r_\circ}{(2\pi D)^{1/2}}$

D is the diffusion coefficient of X and for spectroscopic data $\frac{[X]}{[X_\circ]}$ equals $\frac{A}{A_\circ}$, the integrated absorbance ratio.[114]

An extremely critical aspect of the kinetics experiments with diffusion controlled dimerization of matrix-isolated cyclobutadiene was the ability to determine accurate temperatures of the cold tip during one run and to ensure temperature reproducibility between different runs. Accuracy and reproducibility of temperature measurement to better than ± 0.25°K was desirable. Also required was the rapid attainment of a chosen temperature and stability at the "warm-up" temperature. In this author's experience, the most satisfactory experimental combination was that of the closed-cycle helium microrefrigerator (equipped with a 44°K radiation shield) coupled to a proportional temperature controller and a digital microvoltmeter. With this arrangement temperature reproducibility and stability of better than ± 0.1°K could be achieved so long as warm-up times were of the order of 10 sec/°K (ca. 7.5-20°K), of 20 sec/°K (20-30°K) or of 30 sec/°K (30-40°K).

EXPERIMENTAL PROCEDURES FOR THE MATRIX WORK

Purification

In matrix-isolation work, it is crucial that the materials to be used be of very high purity. Traces of oxygen or nitrogen may cause a rare gas matrix to crystallize while any residual water vapour may destroy reagents or mask the infrared spectral regions of 3500-3000 and 1650-1550 cm^{-1} where water absorbs strongly.

Removal of Oxygen

Oxygen was excluded from all samples: organic materials were degassed before use and the matrix gases used were of ultra-high purity.

Degassing of the sample was accomplished in vacuum. The material to be deposited was cooled to 77°K (liq N_2) or 195°K (dry ice-acetone), depending on volatility, and the line was evacuated. Melting of the sample, at room temperature or above removed most of the adsorbed gases. The resulting liquid was recooled to the chosen temperature and evacuation was resumed. With volatile compounds care was taken to minimize loss of compound by sublimation or distillation into the vacuum line. This overall sequence was always repeated at least twice.

Removal of Moisture

Moisture, a common impurity, was adequately removed from the liquid and solid photoprecursors used in this work by storing them in a desiccator over a chemical desiccant. Since these materials are thermally unstable and light and oxygen sensitive, they were kept under an argon atmosphere at -20 to -25°C in the dark.* Transferring of the sample to the deposition-line finger was carried out under a stream of argon.

Residual moisture in rare gases was removed by passing the gas through a cold trap. A dry ice-acetone trap was used for xenon; argon was dried through a liquid nitrogen trap.

General Purification

The following paragraphs deal with the methods used to purify the precursors to a degree adequate for isolation within a matrix.

Distillation was usually satisfactory for matrix work provided the process was carried out carefully and no volatile impurities were introduced.

Recrystallization, a popular method for purifying solids, was found to be a poor method for preparing pure solid matrix materials because small amounts of solvent are always occluded in the crystals and, unless the solvent was volatile enough to be completely removed by degassing, it was co-deposited with the sample and caused stray spectral effects.

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* These desiccator containers were never opened in air while still cold.

Vacuum sublimation provided samples free of volatile components and when used in conjunction with recrystallization, very pure samples were obtained.

Preparative gas chromatography provided pure samples of volatile substances. The product was collected in a U-tube cooled to the appropriate temperature (see Table 10). Care was taken not to condense volatile impurities while collecting the pure sample and the U-trap was kept under an inert atmosphere at all times.

Details of the experimental variables for each procedure are given in table form in the following pages. Descriptions of the procedures have been presented in the preceding sections.

TABLE 10

CONSTANT TEMPERATURE BATHS[93]

Temperature (°C)	Slush or Bath[a]
0	Ice-water[a]
0 to -20	Ice-NaCl, HCl, or $CaCl_2$ solution[a]
-9	Methyl salicylate
-12.0	*t*-Amyl alcohol
-14.0	Benzaldehyde
-15.3	Benzyl alcohol
-22.9	Carbon tetrachloride[a]
-33 to -45	Liquid ammonia
-35.6	Ethylene dichloride
-45.2	Chlorobenzene
-50.0	Ethyl malonate
-63.5	Chloroform[a]
-73.5[b]	Dry ice-acetone
-83.6	Ethyl acetate
-95.0	Toluene
-96.7	Methylene chloride
-97.8	Methanol
-111.6	Carbon disulfide
-119.0	Ethyl bromide[a]
-126.3	Methylcyclohexane
-131.5	*n*-pentane
-138.7	Ethyl chloride
-150	Chloroform, 18.1%[a]; ethylbromide, 41.3%; ethyl chloride, 8.0%; *trans*-1,2-dichloroethylene, 12.7%; and trichloroethylene, 19.9%
-160.5	Isopentane
-183[b]	Liquid oxygen
-185.7[b]	Liquid argon
-196[b]	Liquid nitrogen[a]

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[a] Nonflammable.

[b] Temperature dependent on atmospheric pressure.

Cyclobutadiene-h_4 (1) from 12-Oxa-tetracyclo[4.4.3.0.0^{2,5}]trideca-3,7,9-triene (23a) Isolated in an Argon Matrix

a) Cooling of the Target.

Pressure in the cryostat: 2×10^{-6} Torr

Temperature controller setting: 220.00 Ω,
Germanium sensor

Cooling time: 105 min

Temperature read-out: 10-15°K (potentiometer)

b) Deposition of the Matrix-Precursor Mixture.

Substrate temperature: "finger", 40-50°C
line, room temperature

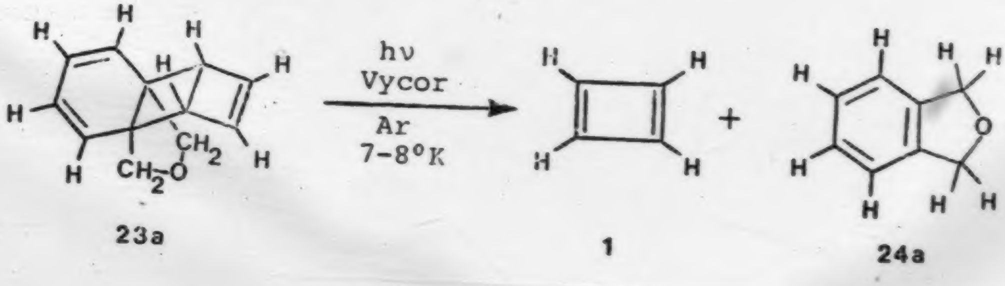
Deposited: 12.7 Torr of Argon in 80 min
(Table 11, Figure 38)

c) Photolysis of the Matrix-Isolated Precursor.

Lamp: low pressure mercury vapor.

Filter: Vycor

The progress of the photolysis was monitored by infrared spectroscopy, Figure 39 (Nicolet FT-IR Interferometer)



23a 1 24a

Irradiation Time (min)	Line Position (cm^{-1})	Integrated Absorbance (cm^{-1}) x 10^3	Relative Intensity
30	1523.3	27.6	1.3
	1239.9	835.8	40.2
	723.5	251.3	12.1
	572.4	2,077.2	100.0
75	1523.3	38.8	1.4
	1239.9	1,204.4	44.0
	723.4	300.0	11.0
	572.4	2,735.1	100.0
120	1522.8	52.2	1.5
	1239.9	1,348.6	39.1
	723.4	488.6	14.1
	572.3	3,448.4	100.0

	Line Position (Average)	Relative Intensity (Average)
A	1523	1.4
B	1240	41.1
C	723	12.4
D	572	100.0

d) Warm-up Diffusion Study.

The temperature of the Displex cold-tip was gradually increased form 7-8°K to 35°K. The effects of the warming on the composition of the matrix were also monitored by infrared spectroscopy, Figure 40 (Nicolet FT-IR Interferometer).

Warm-up Time (min)	Line Position (cm^{-1})	Integrated Absorbance (cm^{-1}) x 10^3	Relative Intensity
60 (28°K)	1522.9	51.0	1.5
	1239.8	1,240.0	36.4
	723.3	480.0	14.1
	572.2	3,400.0	100.0
60 (33°K)	1522.5	44.8	1.5
	1239.9	1,173.0	39.3
	723.6	381.8	12.8
	572.1	2,981.8	100.0
60 (35°K)	1522.4	30.2	1.5
	1241.7	810.6	40.3
	724.0	204.5	10.1
	573.6	2,009.4	100.0
90 (35°K)	1522.4	19.2	1.1
	1242.8	666.1	39.7
	724.0	163.7	9.7
	573.8	1,677.3	100.0

The integrated absorbances of bands $\underset{\sim}{A}$-$\underset{\sim}{D}$ during irradiation and warm-up are graphically represented in Figure 41.

				Cold Tip Temperature		
Time	**Reservoir Pressure**	**Flow Rate**	**Line Pressure**	**Controller**	**Readout**	**Cryostat Pressure**
	(Torr)	(SCC/min, flow meter)	(Torr)	(Ω)	(°K)	(Torr)
12.00	30.2	0.0-2.6	0.0-3.2	220.00	10-15	5×10^{-8}
12.10	27.6	2.5-2.7	2.9	"	"	1×10^{-7}
12.25	25.7	2.7	2.9	"	"	5×10^{-7}
1.10	19.6	2.5-2.7	2.9	"	"	2×10^{-6}
1.20	17.5	2.6	2.9	"	"	5×10^{-6}

TABLE 11

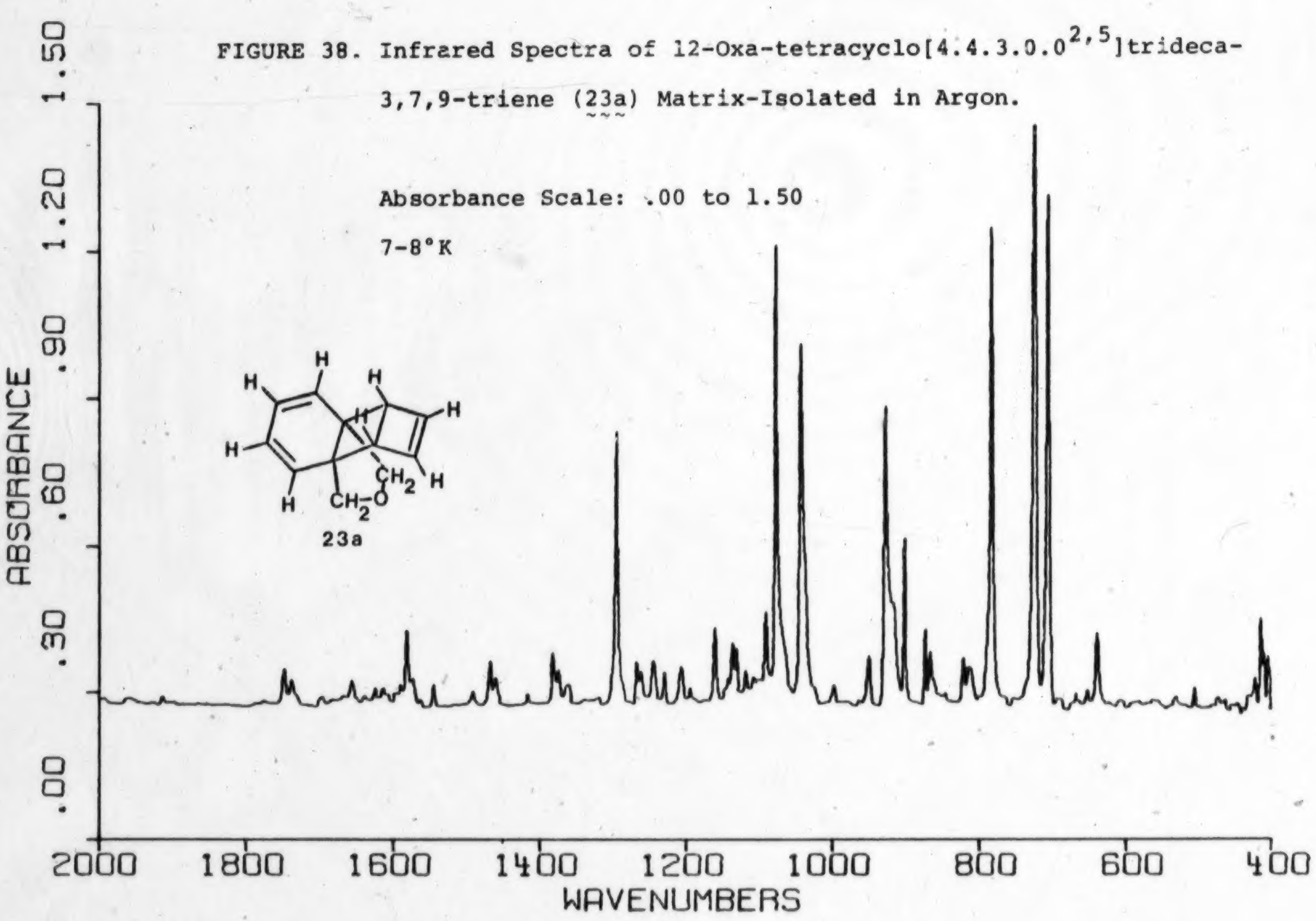


FIGURE 38. Infrared Spectra of 12-Oxa-tetracyclo[4.4.3.0.0^{2,5}]trideca-3,7,9-triene (23a) Matrix-Isolated in Argon.

Absorbance Scale: .00 to 1.50

7-8°K

23a

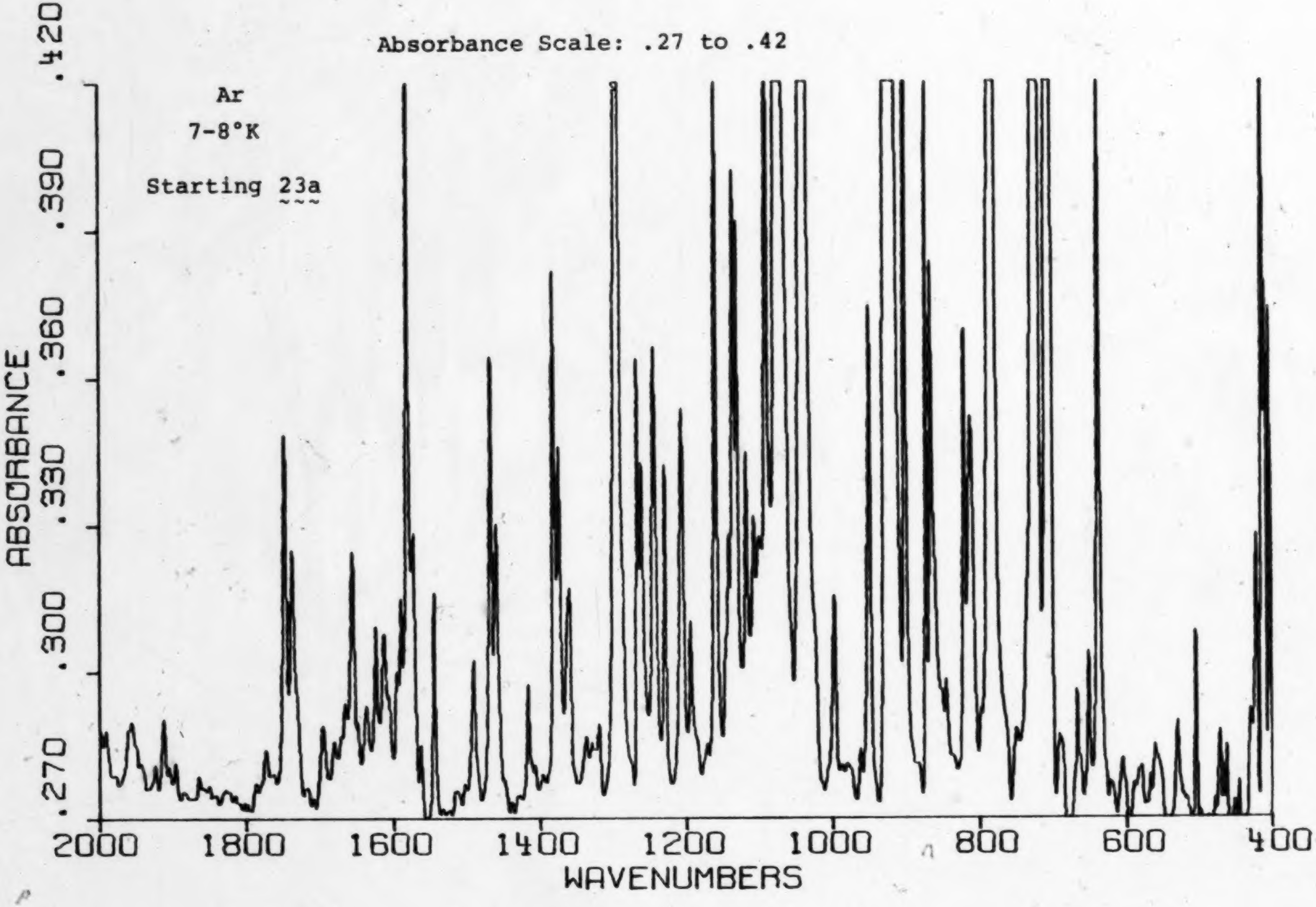
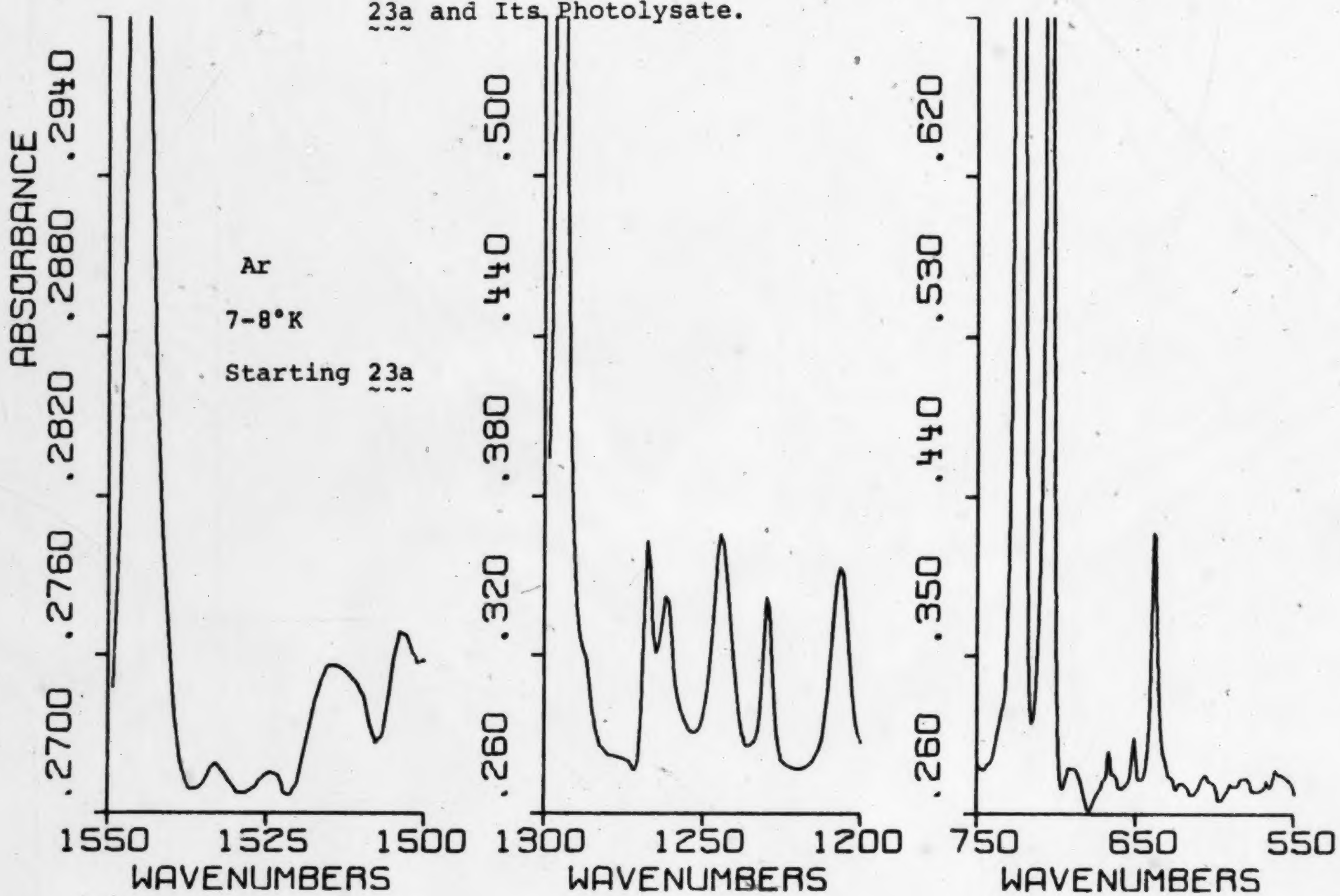
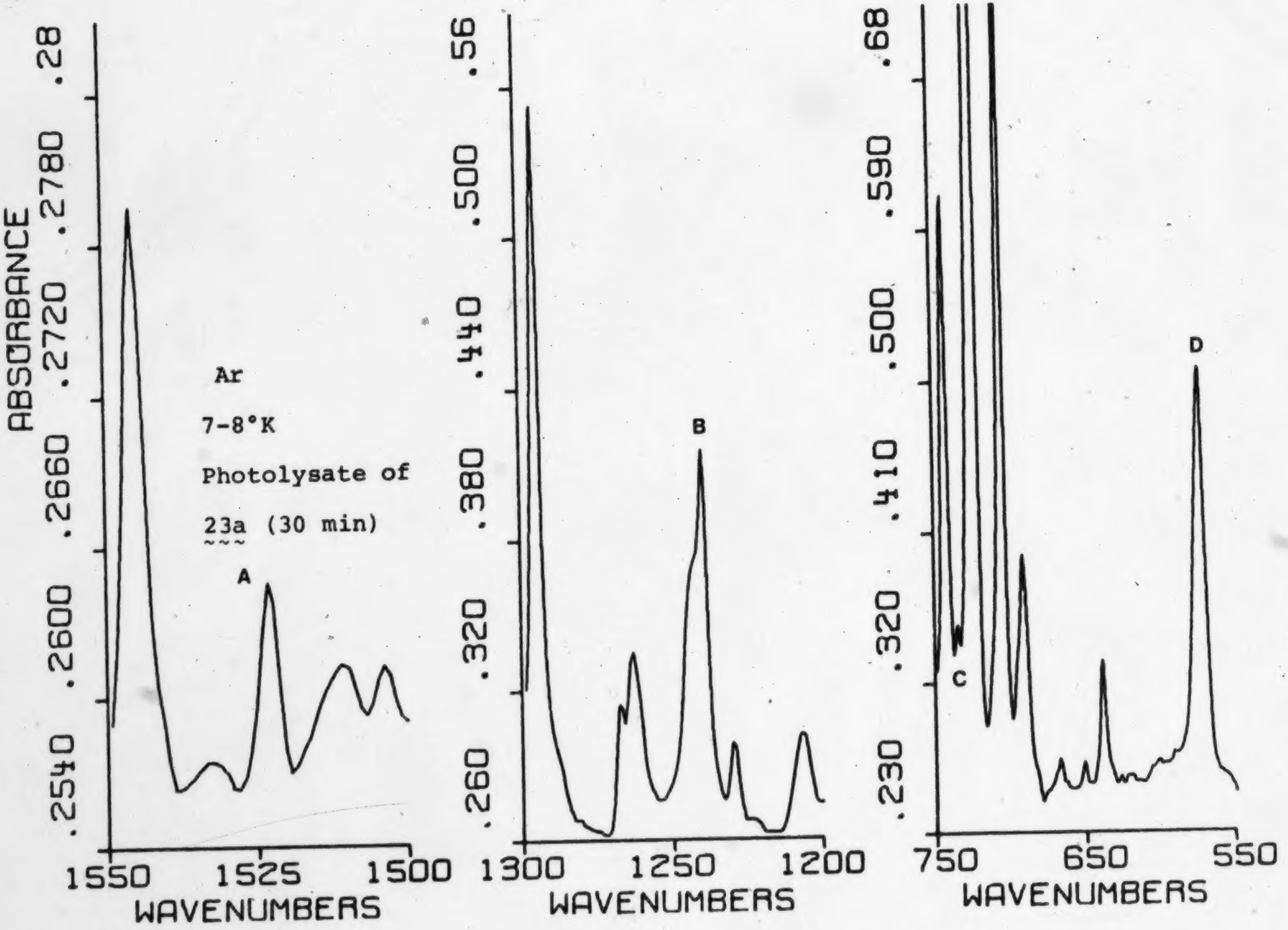

Absorbance Scale: .27 to .42
Ar
7-8°K
Starting 23a
ABSORBANCE
.270
.300
.330
.360
.390
.420
2000
1800
1600
1400
1200
1000
800
600
400
WAVENUMBERS

FIGURE 39. Selected Regions of the Infrared Spectra of Matrix-Isolated **23a** and Its Photolysate.

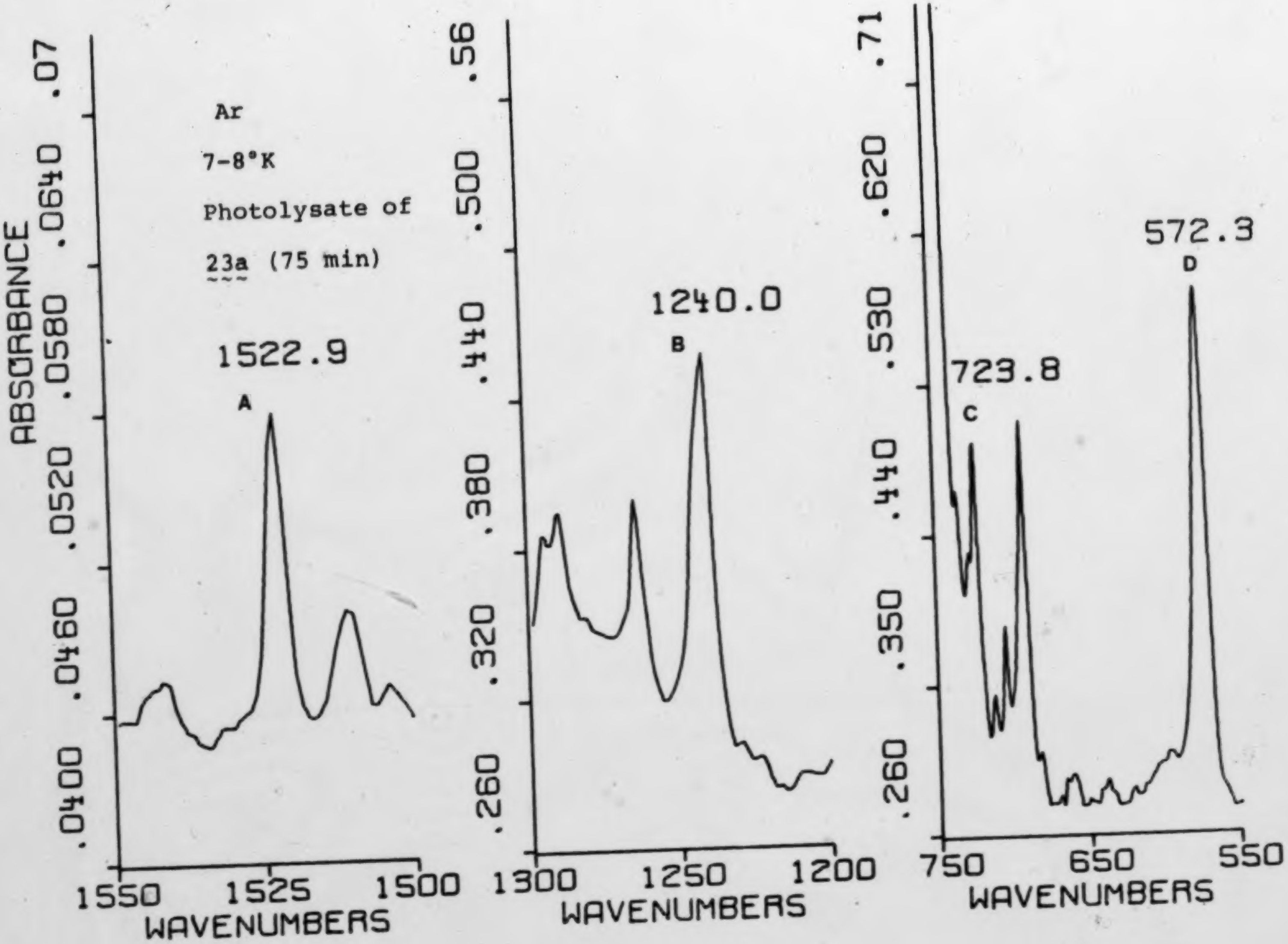



Ar

7-8°K

Photolysate of

23a (30 min)


Ar
7-8°K
Photolysate of
23a (75 min)
ABSORBANCE
.0400
.0460
.0520
.0580
.0640
.07
1522.9
A
1550
1525
1500
WAVENUMBERS
.260
.320
.380
.440
.500
.56
1240.0
B
1300
1250
1200
WAVENUMBERS
.260
.350
.440
.530
.620
.71
723.8
C
572.3
D
750
650
550
WAVENUMBERS

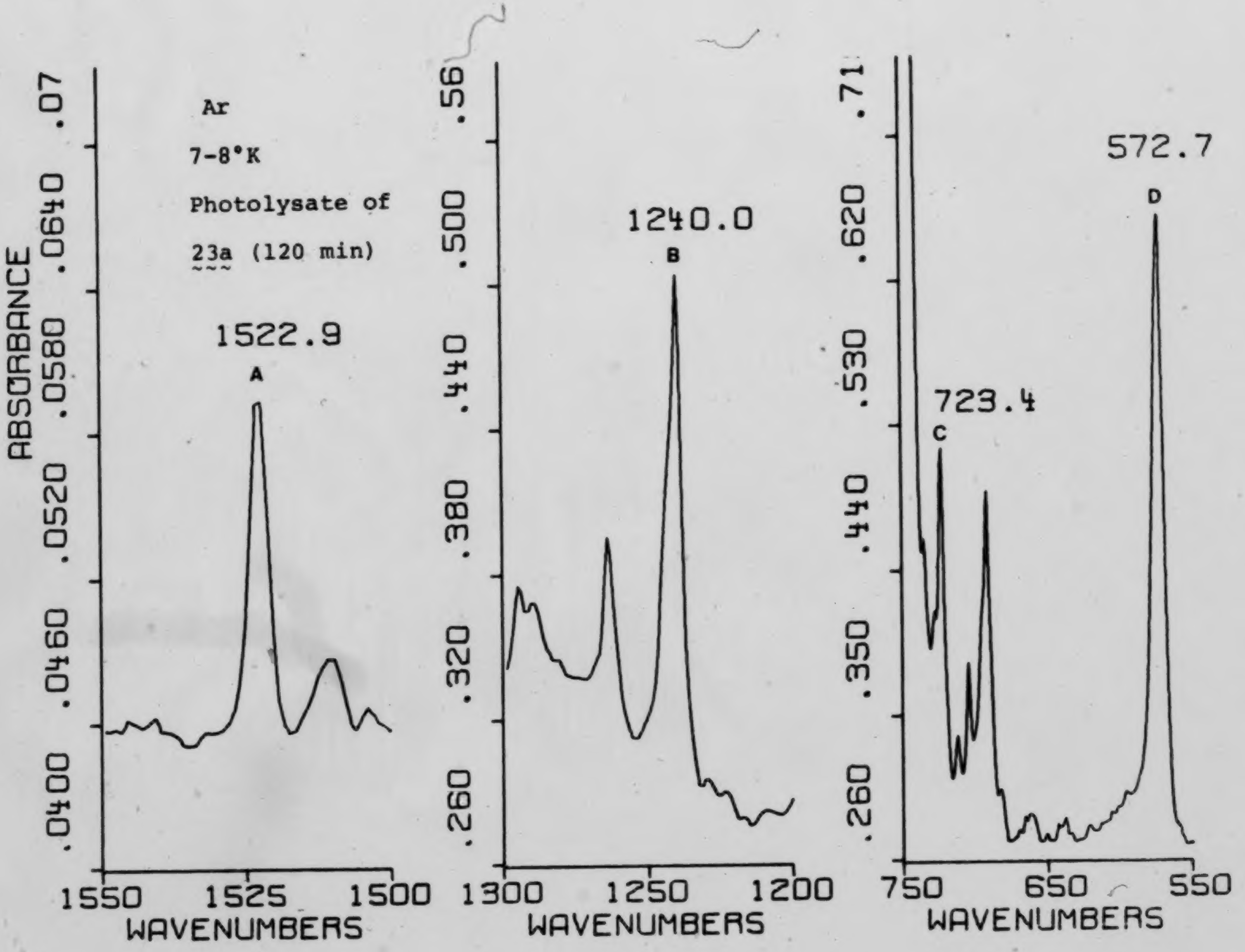
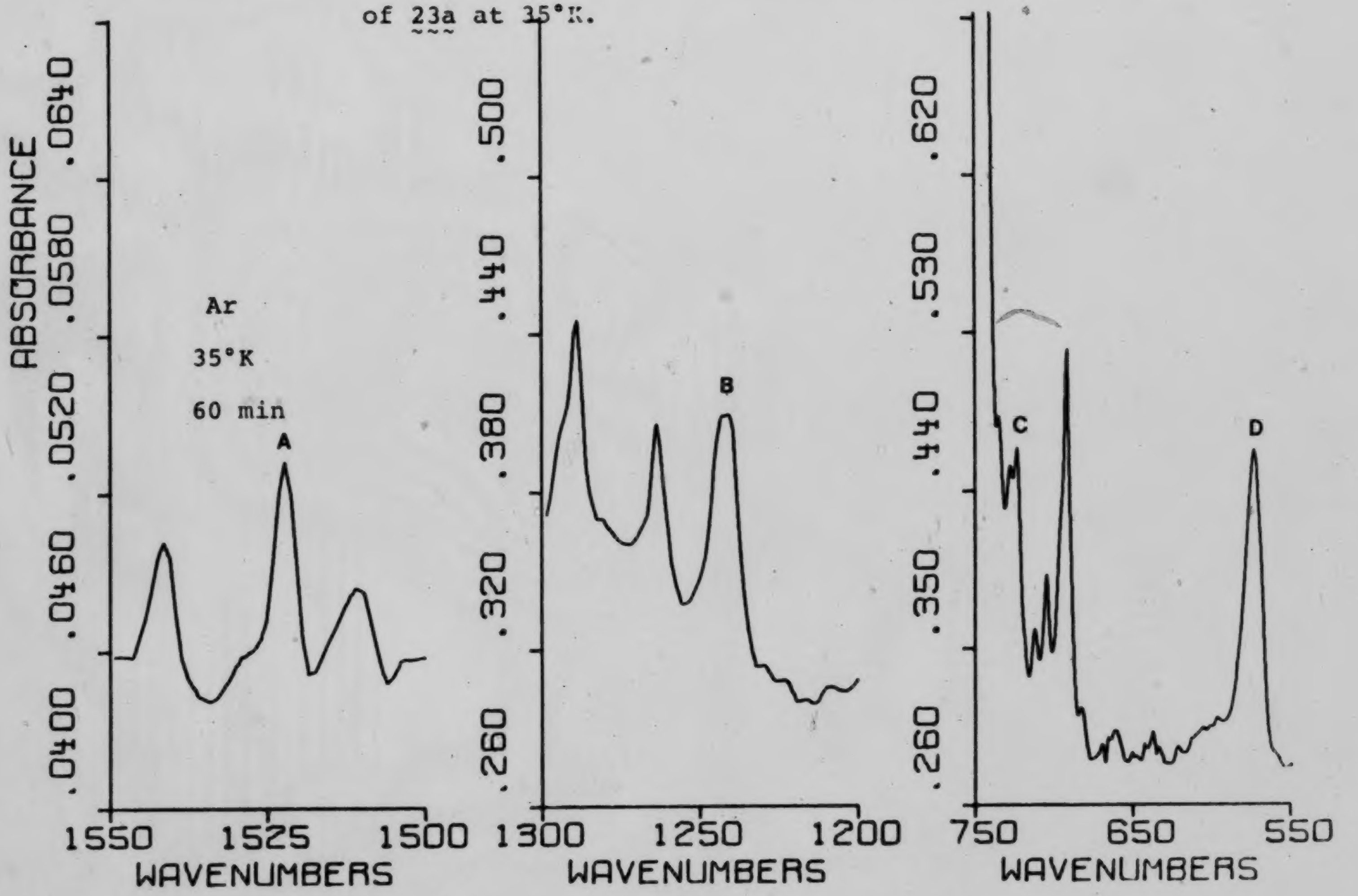
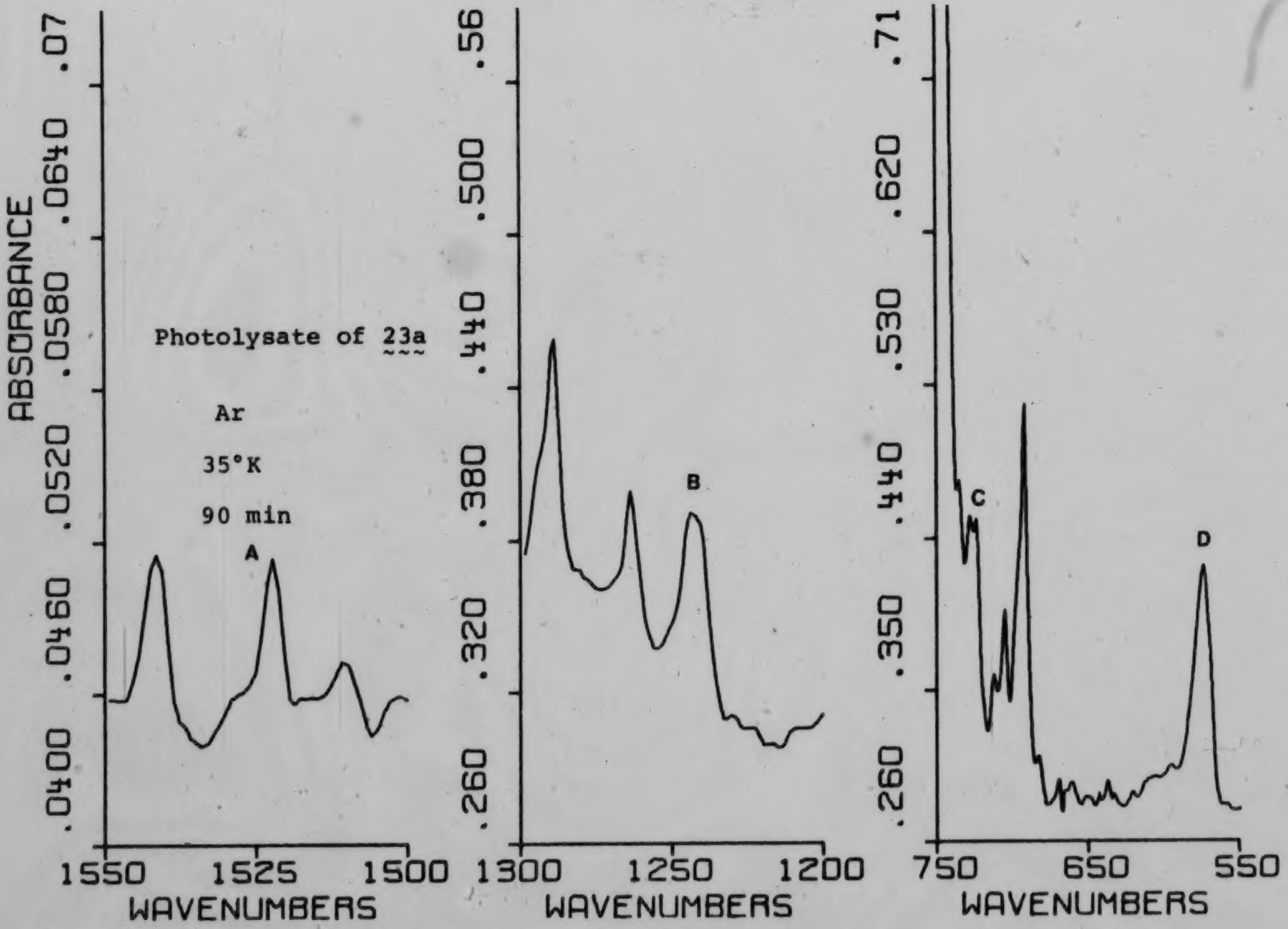

ABSORBANCE
.0400
.0460
.0520
.0580
.0640
.07
Ar
7-8°K
Photolysate of
23a (120 min)
1522.9
A
1550
1525
1500
WAVENUMBERS
.260
.320
.380
.440
.500
.56
1240.0
B
1300
1250
1200
WAVENUMBERS
.260
.350
.440
.530
.620
.71
723.4
C
572.7
D
750
650
550
WAVENUMBERS

FIGURE 40. Selected Regions of the Infrared Spectra of the Photolysate of **23a** at 35°K.





Photolysate of 23a

Ar

35°K

90 min

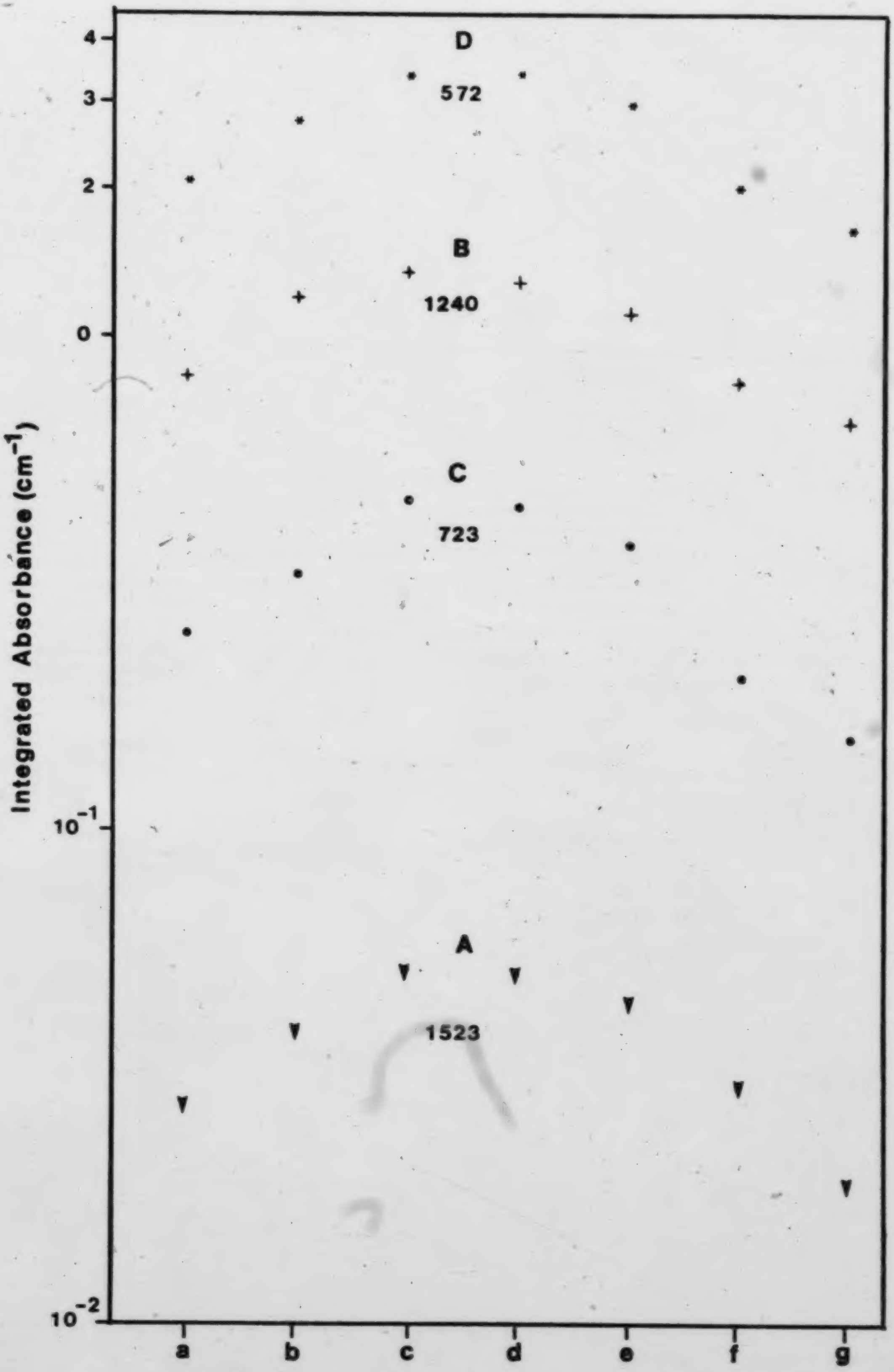
Irradiation (overall time)

- a) 30 min
- b) 75 min
- c) 120 min

Warming

- d) 28°K (60 min)
- e) 33°K (60 min)
- f) 35°K (60 min)
- g) 35°K (90 min)

FIGURE 41. Intensities of the Infrared Bands **A**-**D** During Irradiation and Warming (Photoprecursor **23a**). The Integrated Absorbance (cm^{-1}) is Expressed in Logarithmic Scale.


Integrated Absorbance (cm^{-1})
4
3
2
0
10^{-1}
10^{-2}
D
572
B
1240
C
723
A
1523
a
b
c
d
e
f
g

Cyclobutadiene-$\underline{d}_4$ (28) from 12-Oxa-tetracyclo-[4.4.3.0.0^{2,5}]trideca-3,7,9-triene-2,3,4,5,7,8,9,10-$\underline{d}_8$ (31b) Isolated in an Argon Matrix

a) Cooling of the Target.

Pressure in the cryostat: 6 x 10^{-6} Torr

Temperature controller setting: 220.00 Ω, Germanium sensor

Cooling time: 60 min to 77°K, 75 min to 10°K

Temperature read-out: 10-15°K (potentiometer)

b) Deposition of the Matrix-Precursor Mixture.

Substrate ("finger") and line at room temperature

Deposited: 15.1 Torr of Argon in 120 min

(Table 12, Figure 42)

c) Photolysis of the Matrix-Isolated Precursor.

Lamp: low pressure mercury vapor

Filter: Vycor

The progress of the photolysis was monitored with the Nicolet FT-Infrared Spectrophotometer (Figure 43).

Irradiation Time (min)	Line Position (cm^{-1})	Integrated Absorbance (cm^{-1}) x 10^3	Relative Intensity
90	1456.0	68.6	2.8
	1043.1	480.4	19.7
	609.3	398.8	16.4
	420.5	2,431.9	100.0
270	1456.0	94.9	3.0
	1043.1	702.1	22.3
	609.2	505.0	16.0
	421.3	3,148.7	100.0

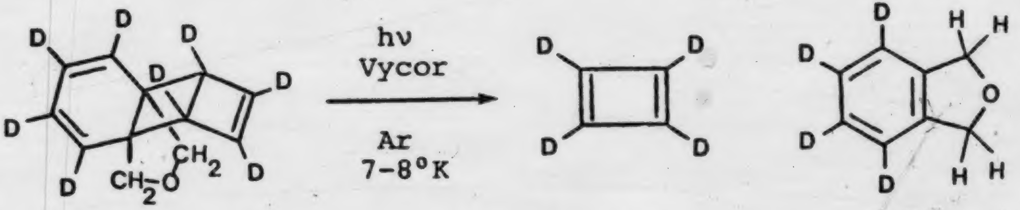
	Line Position (Average)	Relative Intensity (Average)
A'	1456	2.9
B'	1043	21.0
C'	609	16.2
D'	421	100.0

d) Warm-up Diffusion Study.

The temperature of the matrix was increased gradually from 7-8°K to 35°K. The effects of the warming on the photolysate were monitored by infrared spectroscopy, Figure 44 (Nicolet Interferometer).

Warm-up Time (min)	Line Position (cm^{-1})	Integrated Absorbance (cm^{-1}) x 10^3	Relative Intensity
60 (25°K)	1455.6	82.8	2.8
	1043.5	700.0	23.3
	609.5	495.0	16.5
	420.0	3,000.0	100.0
60 (34°K)	1455.2	75.7	3.0
	1043.4	570.0	22.8
	609.4	400.0	16.0
	421.2	2,499.0	100.0
60 (35°K)	1455.1	57.5	2.9
	1043.5	405.0	20.5
	609.7	321.0	16.2
	421.3	1,970.8	100.0
90 (35°K)	1455.0	48.8	3.1
	1043.6	332.0	21.3
	609.8	245.0	15.7
	421.5	1,552.0	100.0
120 (35°K)	1455.8	27.7	3.1
	1043.7	225.0	25.3
	610.3	147.0	16.5
	421.5	890.1	100.0

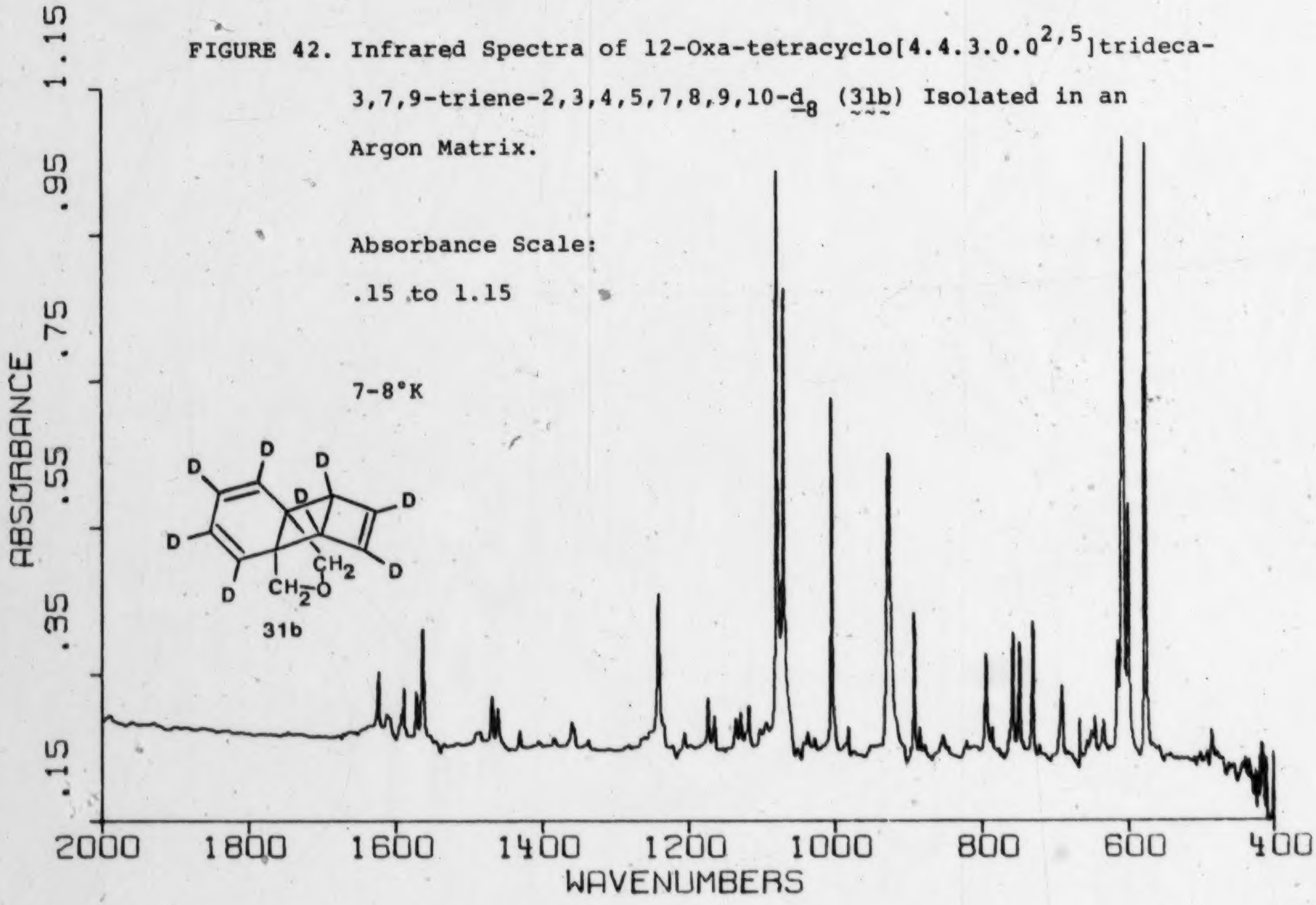
The intensities (integrated absorbances) of bands A'-D' on irradiation and upon warm-up are graphically represented in Figure 45.


D
CH2
CH2
O
hν
Vycor
Ar
7-8°K
H
O

31b 28 24b

				Cold Tip Temperature		
Time	**Reservoir Pressure** (Torr)	**Flow Rate** (SCC/min, flow meter)	**Line Pressure** (Torr)	**Controller** (Ω)	**Readout** (°K)	**Cryostat Pressure** (Torr)
1.15	30.6	3.5-2.5	0-3.0	220.00	10-15	3×10^{-8}
1.30	28.8	2.5	2.8	"	"	2×10^{-7}
1.45	27.0	2.5	2.9	"	"	5×10^{-7}
2.00	25.2	2.4-2.6	2.8	"	"	3×10^{-6}
2.20	22.6	2.6	3.0	"	"	5×10^{-6}
2.30	20.9	2.4-2.6	2.8	"	"	3×10^{-6}
2.45	19.3	2.3-2.7	2.8	"	"	3×10^{-6}
3.00	17.3	2.4-2.6	2.8	"	"	5×10^{-6}
3.15	15.5	2.5	3.0	"	"	2×10^{-5}

TABLE 12



31b

FIGURE 42. Infrared Spectra of 12-Oxa-tetracyclo[4.4.3.0.0^{2,5}]trideca-3,7,9-triene-2,3,4,5,7,8,9,10-$\underline{d}_8$ (31b) Isolated in an Argon Matrix.

Absorbance Scale:

.15 to 1.15

7-8°K

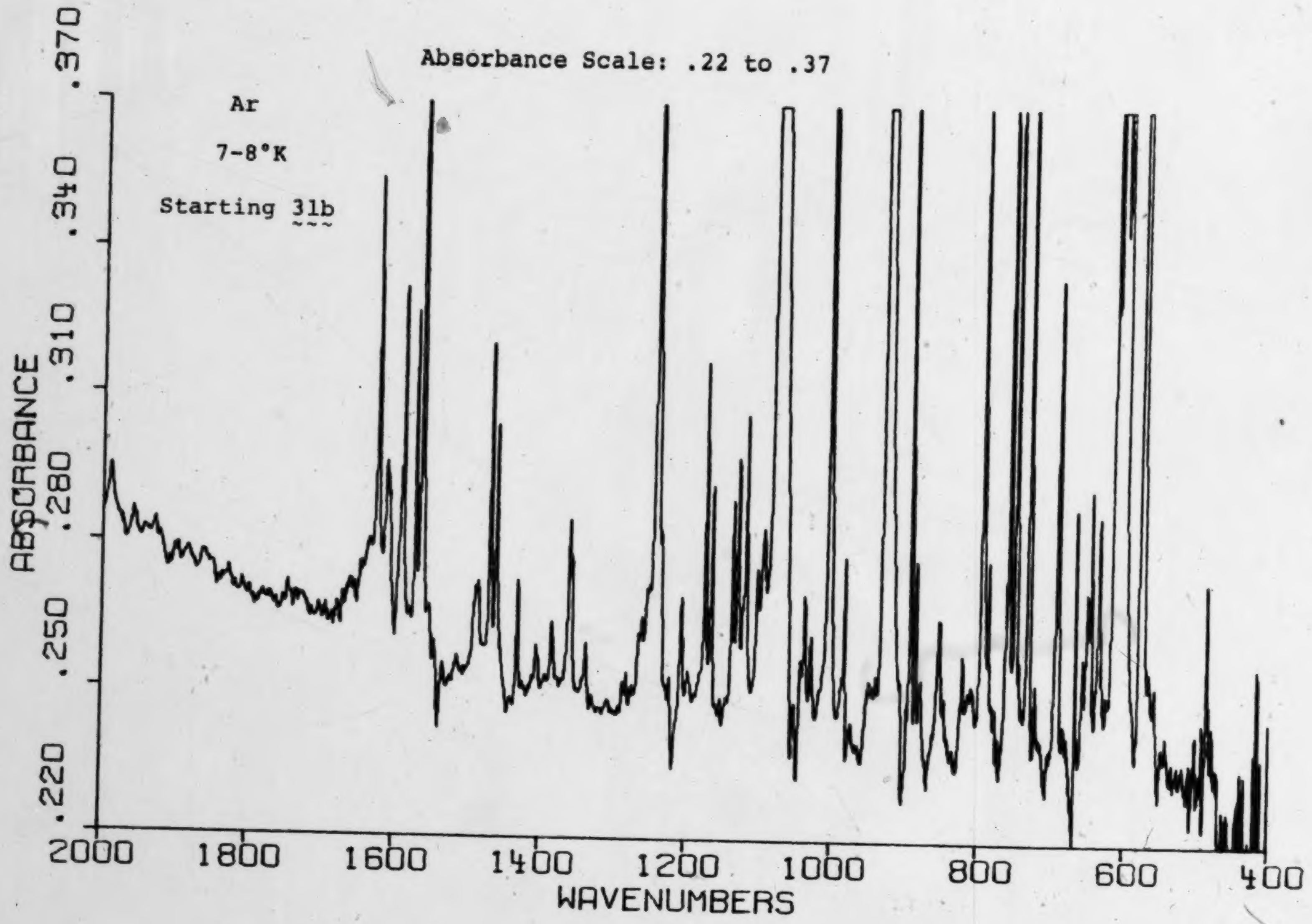
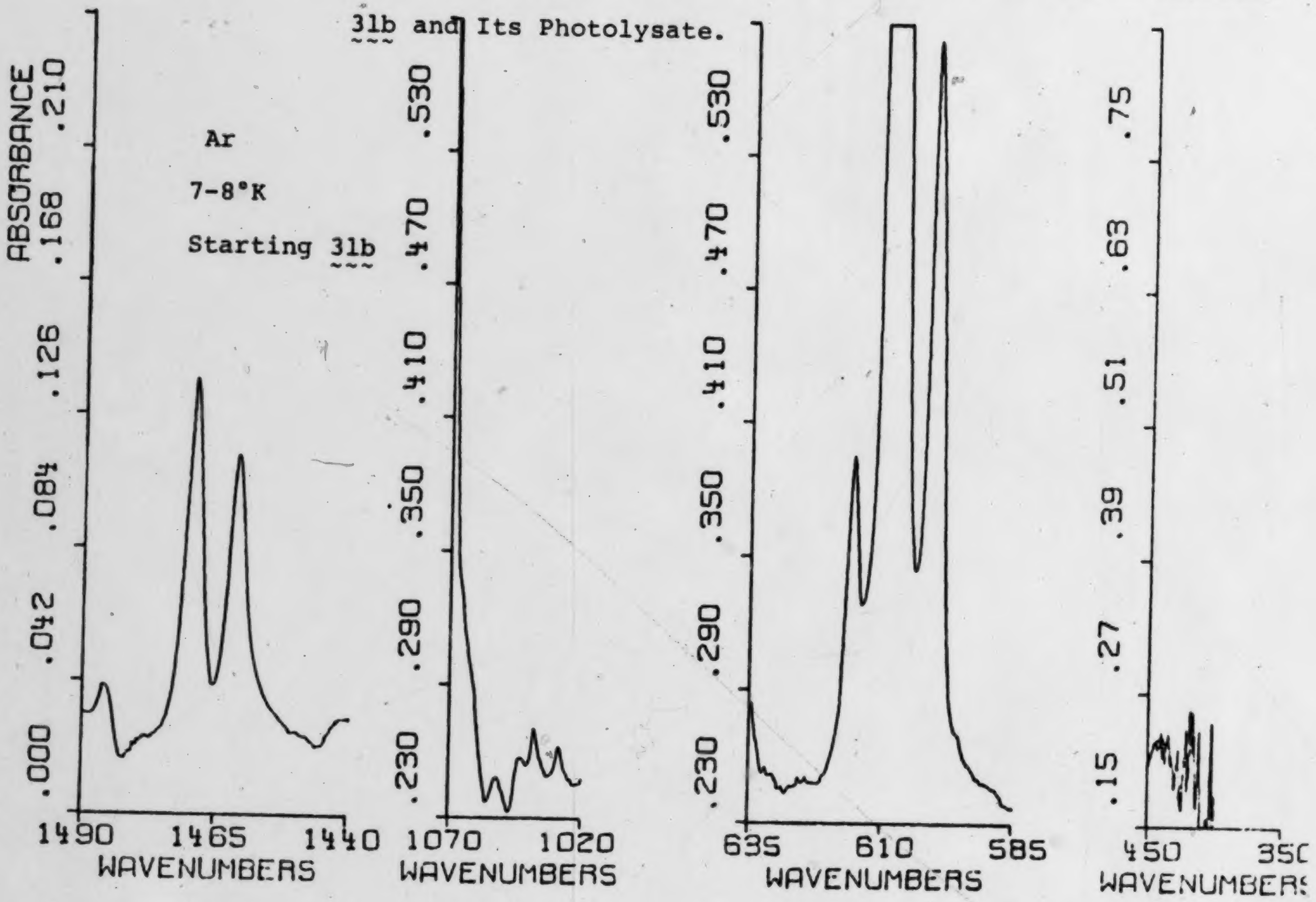
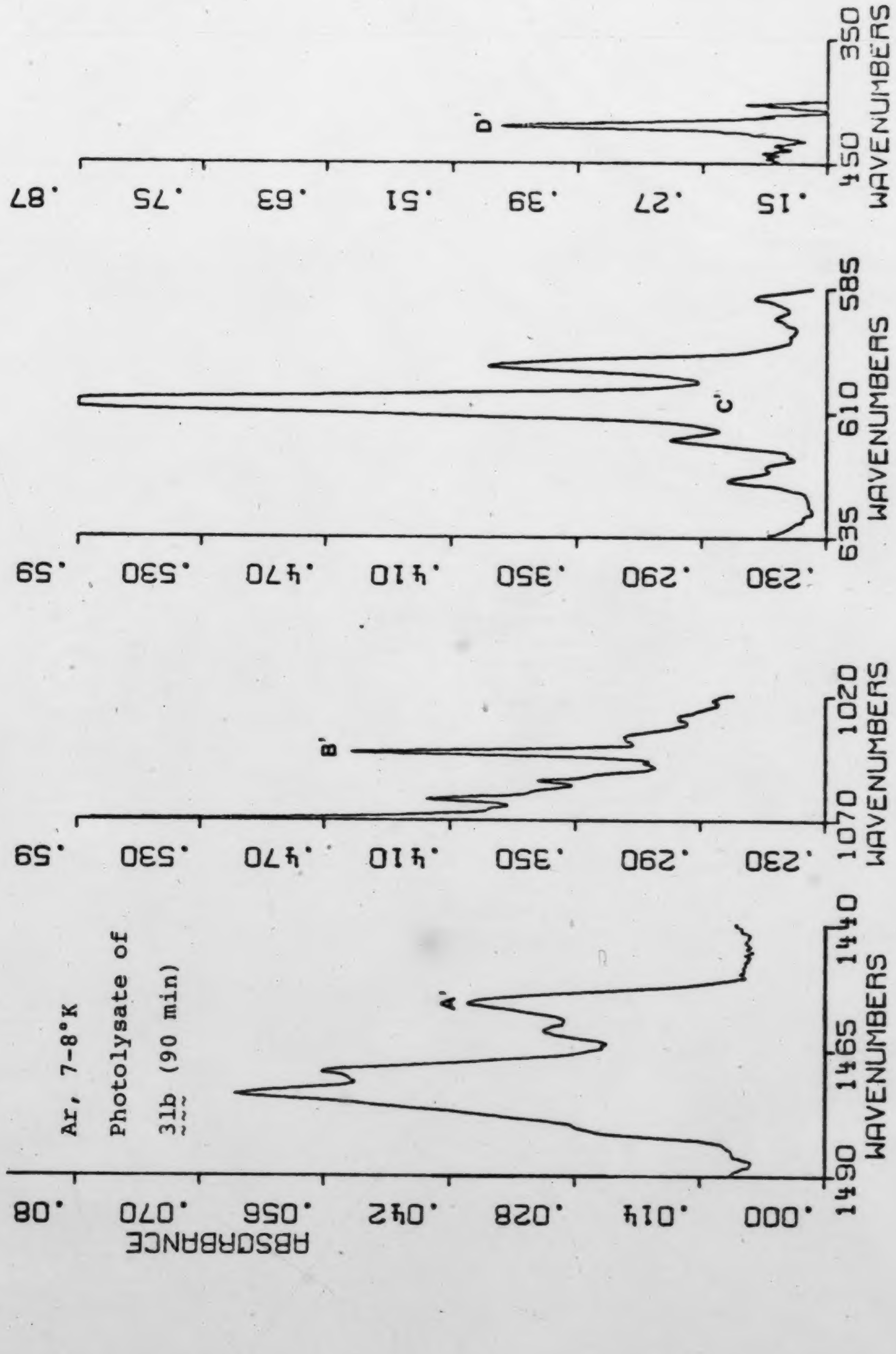

Absorbance Scale: .22 to .37
Ar
7-8°K
Starting 31b
ABSORBANCE
.220
.250
.280
.310
.340
.370
2000
1800
1600
1400
1200
1000
800
600
400
WAVENUMBERS

FIGURE 43. Selected Regions of the Infrared Spectra of Matrix-Isolated **31b** and Its Photolysate.





Ar, 7-8°K

Photolysate of

31b (90 min)

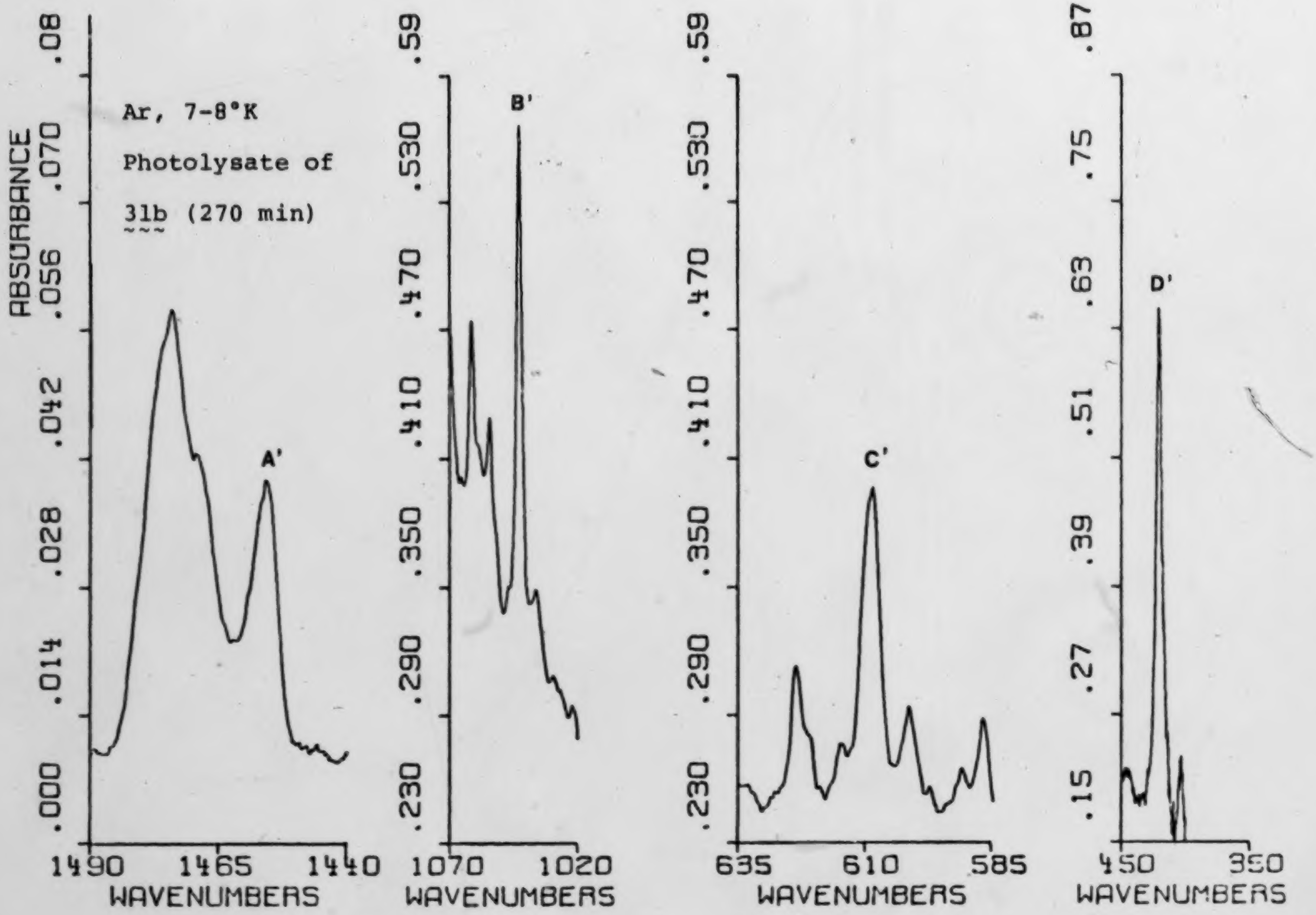
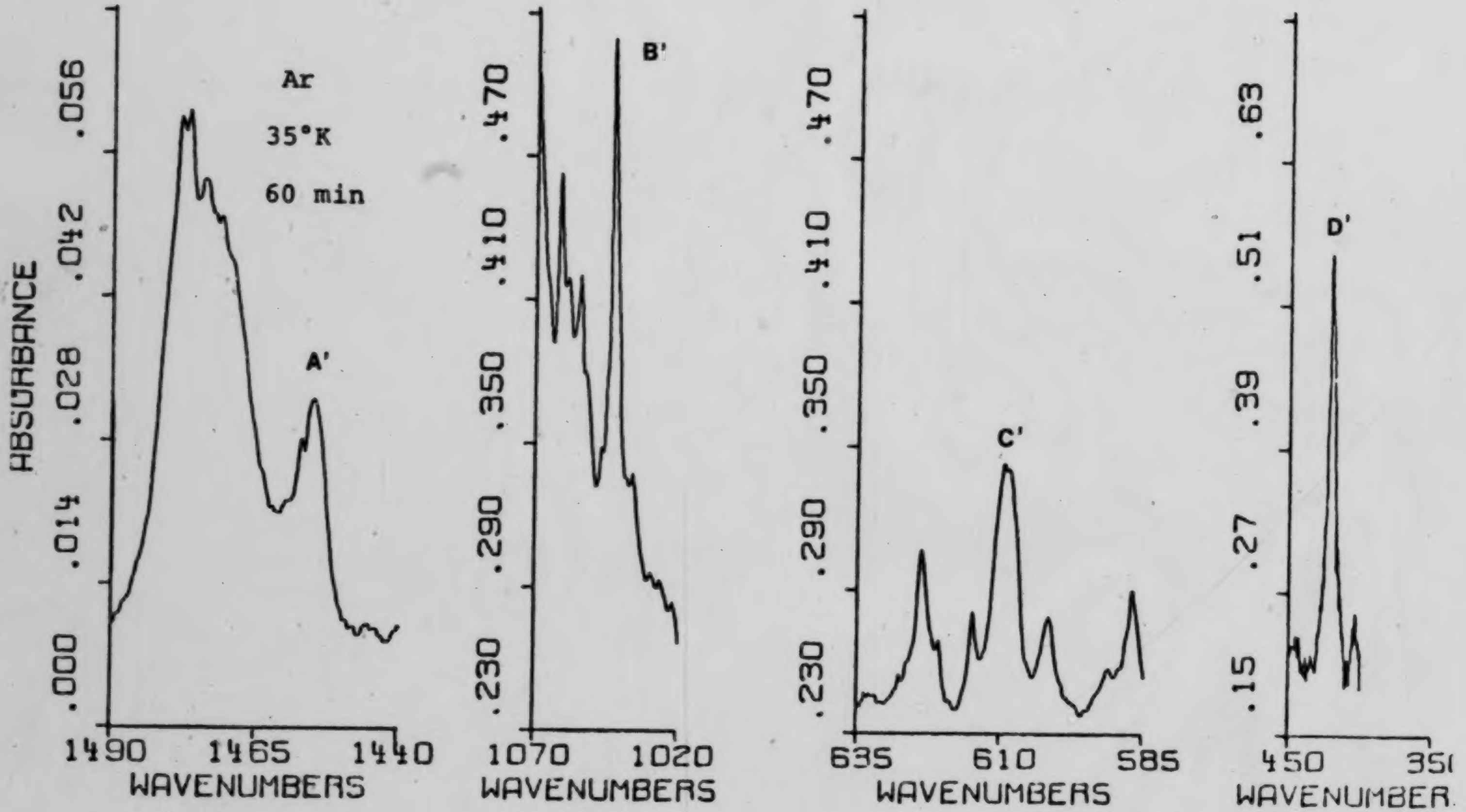
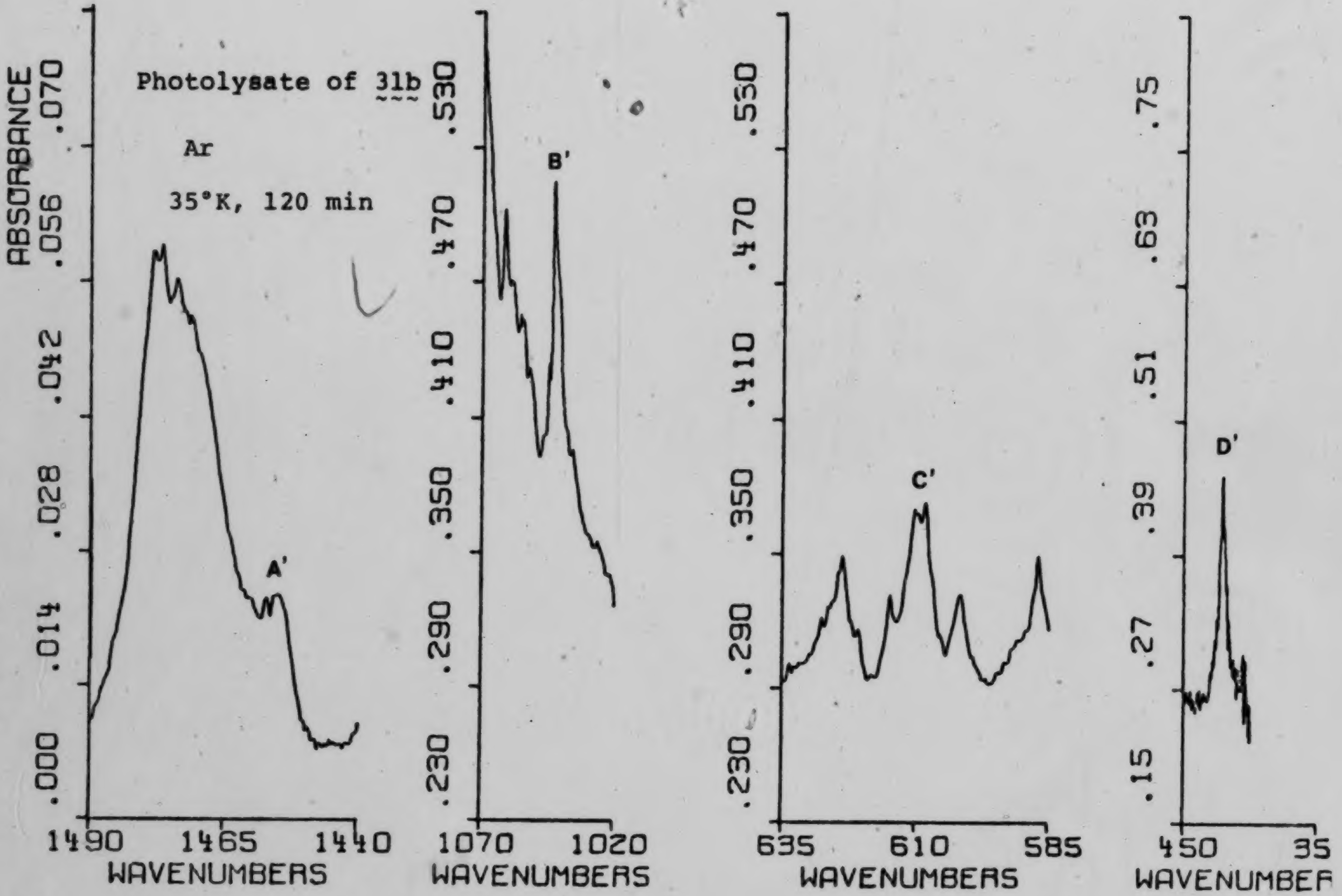

Ar, 7-8°K
Photolysate of
31b (270 min)
ABSORBANCE
.08
.070
.056
.042
.028
.014
.000
1490
1465
1440
WAVENUMBERS
A'
.59
.530
.470
.410
.350
.290
.230
1070
1020
WAVENUMBERS
B'
.59
.530
.470
.410
.350
.290
.230
635
610
585
WAVENUMBERS
C'
.87
.75
.63
.51
.39
.27
.15
450
350
WAVENUMBERS
D'

FIGURE 44. Selected Regions of the Infrared Spectra of the Photolysate of 31b at 35°K.





Photolysate of 31b

Ar

35°K, 120 min

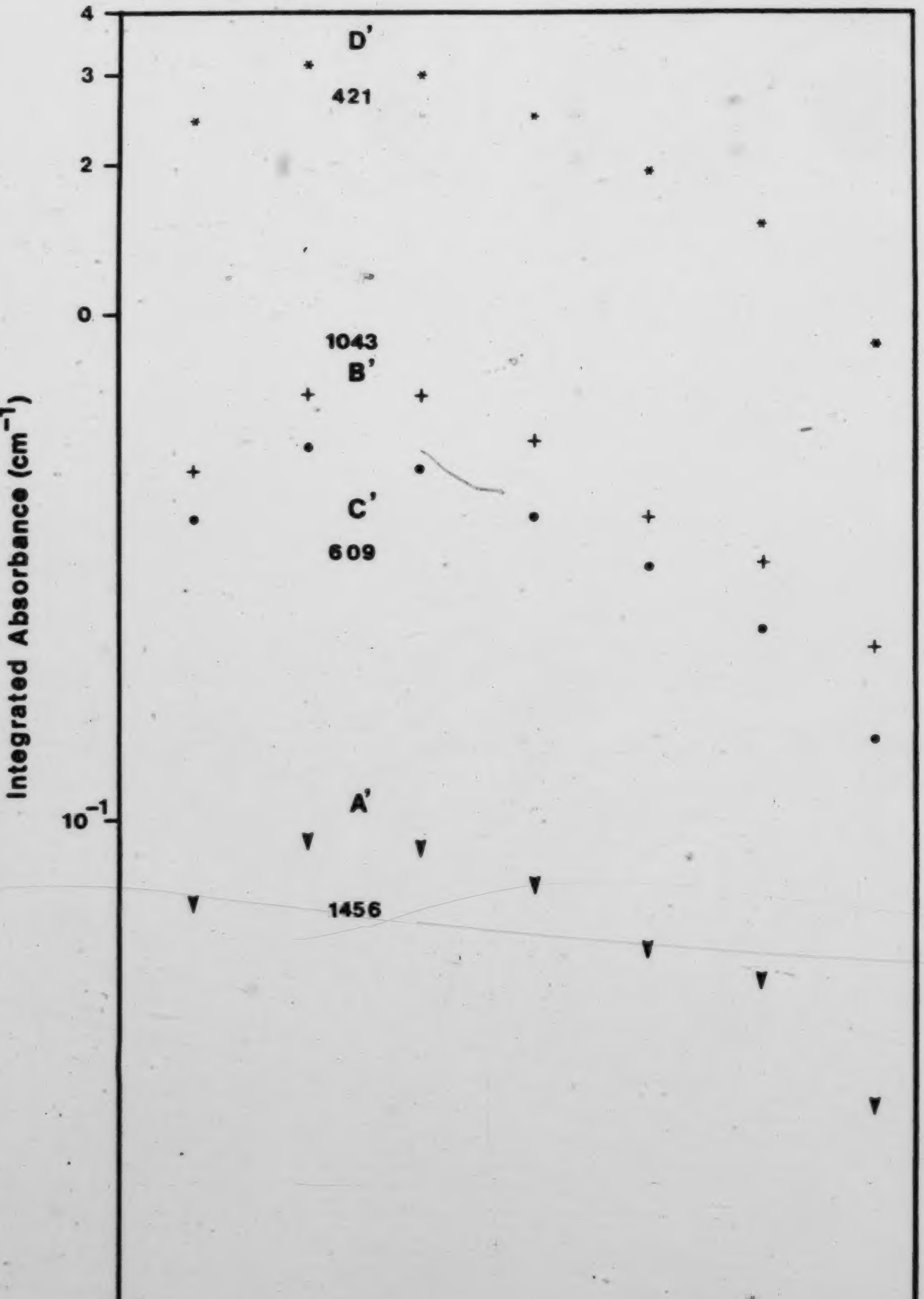
Irradiation (overall time)

a) 90 min
b) 270 min

Warming

c) 25°K (60 min)
d) 34°K (60 min)
e) 35°K (60 min)
f) 35°K (90 min)
g) 35°K (120 min)

FIGURE 45. Intensities of the Infrared Bands A'-D' During Irradiation and Warming (Photoprecursor 31b). The Integrated Absorbance (cm^{-1}) is Expressed in Logarithmic Scale.


Integrated Absorbance (cm^{-1})
4
3
2
0
10^{-1}
10^{-2}
D'
421
1043
B'
C'
609
A'
1456
a
b
c
d
e
f
g

Cyclobutadiene-$\underline{h}_4$(1) from Cyclobutenedicarboxylic Anhydride (25) Isolated in an Argon Matrix

a) Cooling of the Target.

Pressure in the cryostat: 2 x 10^{-7} Torr

Temperature controller setting: 100.00 Ω, Germanium sensor

Heater: 20%

Cooling time: 70 min

Temperature read-out: 180°K (potentiometer)

b) Deposition of the Matrix-Precursor Mixture.

Substrate temperature ("finger surrounded by a water bath): 75-85°C

Line temperature (nichrome heating tape): monitored with a thermocouple at four different positions

Position:	(°C)
1	75
2	75-80
3	80-85
4	85-90

Deposited: 12.1 Torr of Argon in 115 min (Table 13, Figure 46)

c) Photolysis of the Matrix-Isolated Precursor.

Lamps: two medium pressure mercury vapor

Filters: Vycor

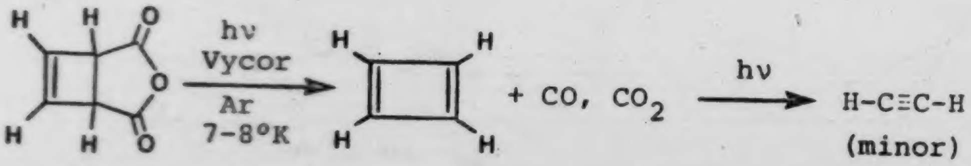
The progress of the photolysis was monitored spectroscopically with the Nicolet FT-Infrared Spectrophotometer (Figure 47)

Irradiation Time (min)	Line Position (cm^{-1})	Integrated Absorbance (cm^{-1}) x 10^3	Relative Intensity
90	1529.6 1528.0	2.4	1.9
	1245.0 1243.4	48.0	39.9
	719.2 717.8	11.3	9.4
	575.5 572.7	120.2	100.0
300	1528.0 1524.6	6.2	2.7
	1245.1 1243.5	88.8	39.2
	721.1 719.5	21.3	9.4
	576.6 575.6	226.3	100.0
450	1529.7 1528.0-1527.2	7.5	1.7
	1245.1 1241.4	168.5	38.1
	721.0 717.9	39.7	9.0
	591.0 576.7	441.6	100.0
630	1529.7 1528.0-1527.3	17.8	2.5
	1245.1 1242.2	274.3	38.4
	720.9 717.8	58.5	8.2
	591.0 576.5	714.5	100.0

	Line Position (Average)	Relative Intensity (Average)
A	1530 1528-1527	2.2
B	1245 1242	38.9
C	721 718	9.0
D	591 576	100.0

d) Warm-up Diffusion Study.

The matrix temperature was increased gradually to about 28°K, then to 32-33°K and finally to 35°K and kept constant till no change could be observed in the infrared spectra.



25

1

Time	Reservoir Pressure (Torr)	Flow Rate (SCC/min, flow meter)	Line Pressure (Torr)	Cold Tip Temperature Controller (Ω)	Cold Tip Temperature Readout (°K)	Cryostat Pressure (Torr)
9.30	33.7	1.8	2.5	100.00	18	2×10^{-8}
9.45	32.3	2.1-2.2	2.5	105.00	17	3×10^{-5}
10.05	30.2	2.2	2.2	108.00	16.5	4×10^{-5}
10.25	27.9	2.5	2.6	110.00	16	2×10^{-5}
11.00	24.1	2.2-2.4	2.5	115.00	15	2×10^{-5}
11.25	21.6	1.9-2.5	2.3-2.5	115.00	15	2×10^{-5}

TABLE 13

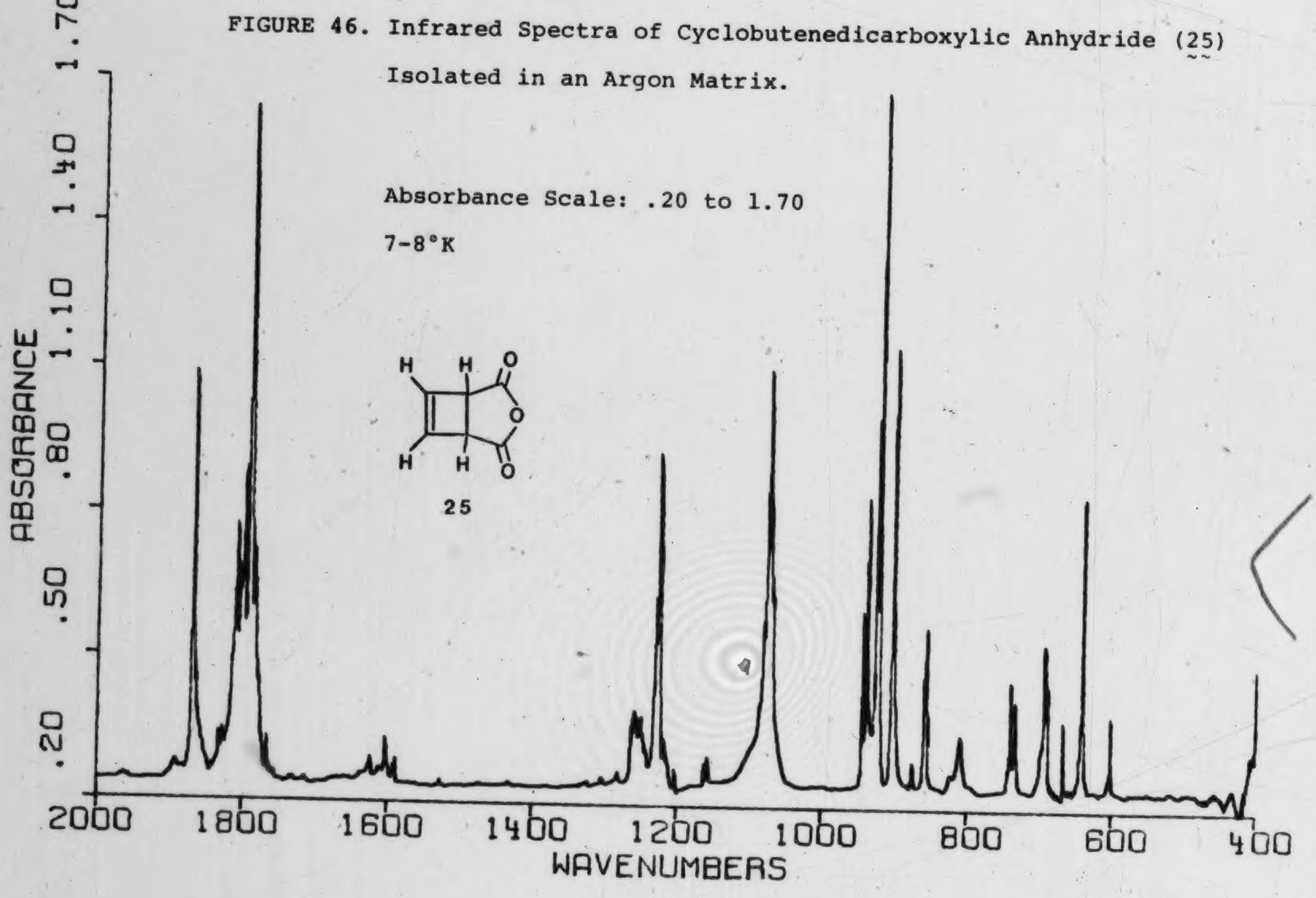


FIGURE 46. Infrared Spectra of Cyclobutenedicarboxylic Anhydride (25) Isolated in an Argon Matrix.

Absorbance Scale: .20 to 1.70

7-8°K

25

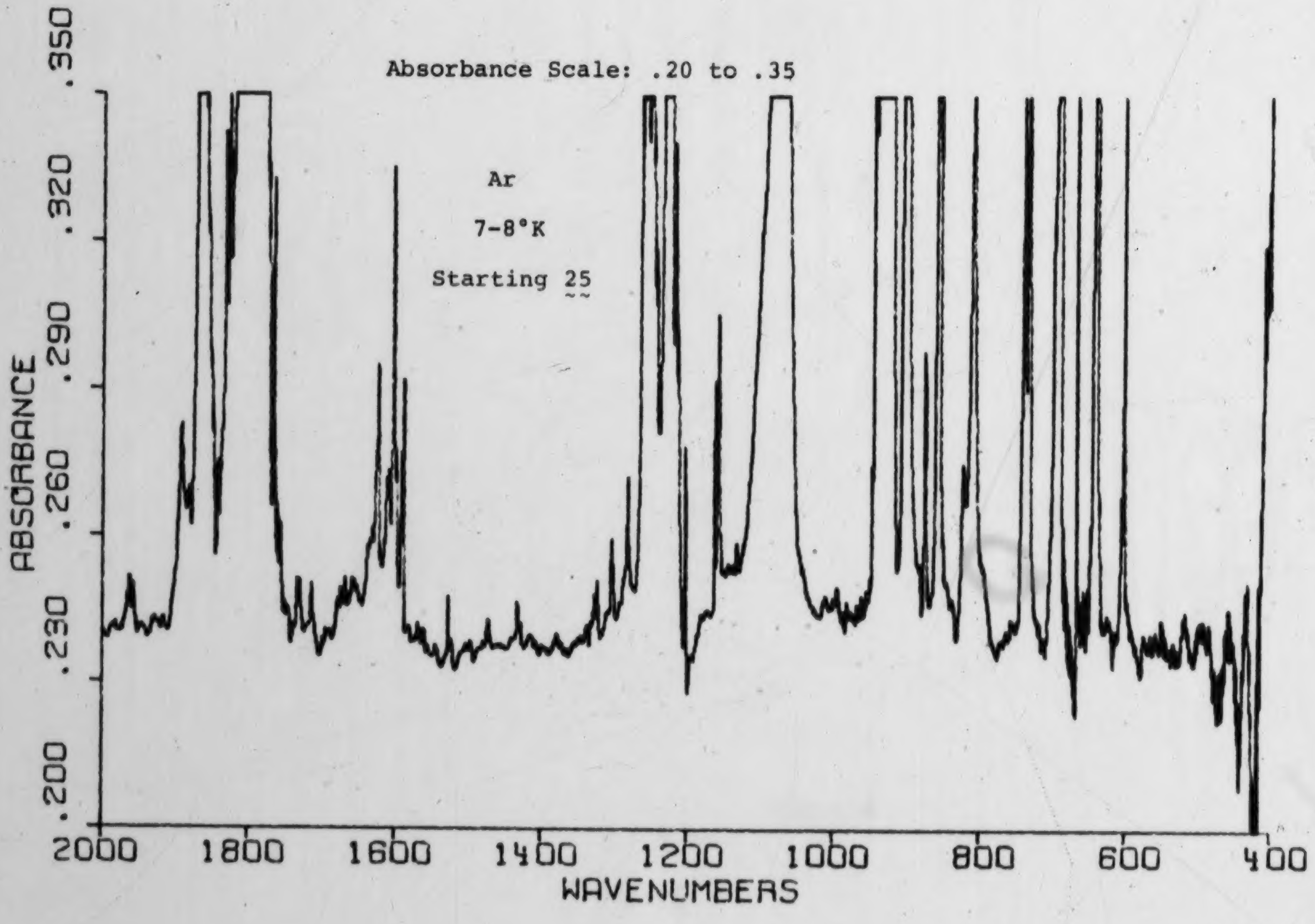
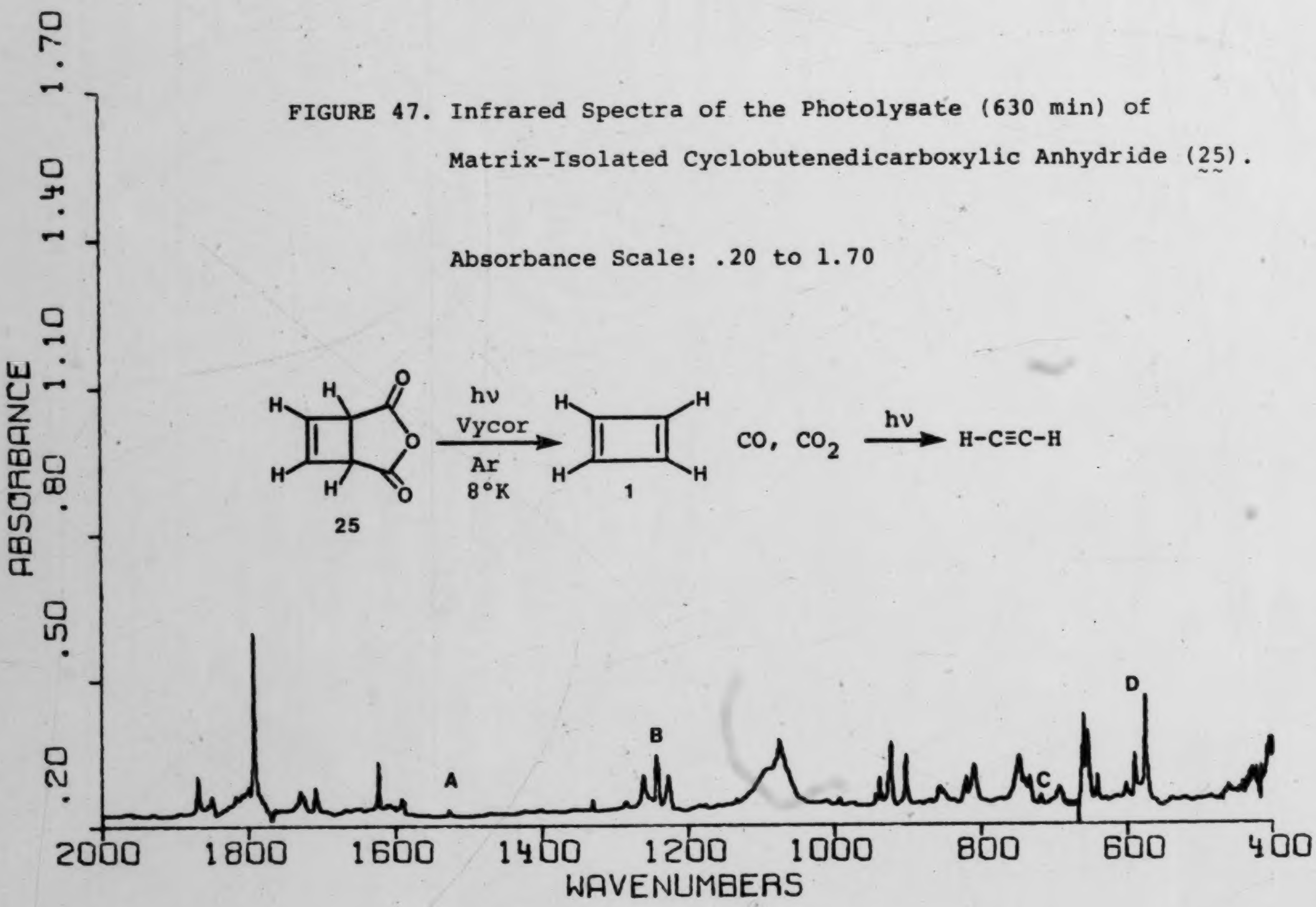
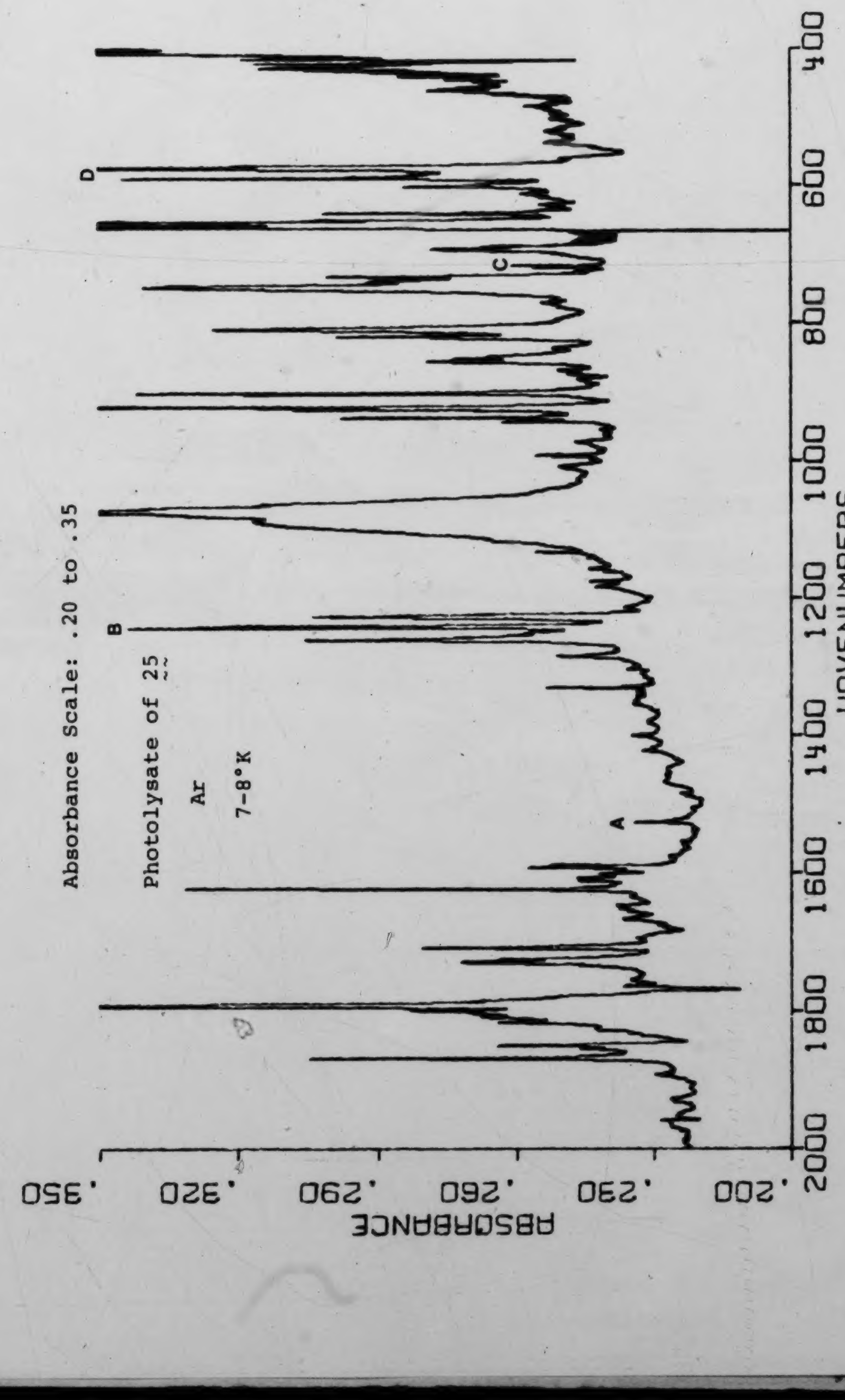

Absorbance Scale: .20 to .35
Ar
7-8°K
Starting 25
ABSORBANCE
.350
.320
.290
.260
.230
.200
2000
1800
1600
1400
1200
1000
800
600
400
WAVENUMBERS

FIGURE 47. Infrared Spectra of the Photolysate (630 min) of Matrix-Isolated Cyclobutenedicarboxylic Anhydride (25).

Absorbance Scale: .20 to 1.70




Absorbance Scale: .20 to .35
Photolysate of 25
Ar
7-8°K
A
B
C
D
ABSORBANCE
.200
.230
.260
.290
.320
.350
WAVENUMBERS
2000
1800
1600
1400
1200
1000
800
600
400

Cyclobutadiene-$\underline{d}_4$ (28) from Cyclobutenedicarboxylic Anhydride-$\underline{d}_4$ (47) Isolated in an Argon Matrix

a) Cooling of the Target.

Pressure in the cryostat: 1×10^{-7} Torr

Temperature controller setting: 100.00 Ω,
Germanium sensor

Heater: 20%

Cooling time: 75 min

Temperature read-out: 16.4°K (digital indicator)

b) Deposition of the Matrix-Precursor Mixture.

Substrate temperature ("finger" surrounded by a water bath): 75-85°C

Line temperature (nichrome heating tape): monitored with a thermocouple at five different positions

Position	(°C)
1	75
2	75-90
3	80
4	90
5	90

Deposited: 20.1 Torr of Argon in 180 min (Table 14, Figure 48)

c) Photolysis of the Matrix-Isolated Precursor.

Lamps: two medium pressure mercury vapor

Filter: Vycor

Irradiation Time (min)	Line Position (cm^{-1})	Integrated Absorbance (cm^{-1}) x 10^{3}	Relative Intensity
165	1464.0 1460.5	5.8	3.9
	1045.9 1044.2	21.3	14.3
	608.0 607.0	48.6	32.7
	432.7 424.5	148.6	100.0
405	1464.1 1460.4	7.5	3.6
	1045.9 1044.2	47.4	22.7
	608.0 607.0	58.1	27.8
	432.5 424.5	209.0	100.0
645	1464.0 1460.3	7.9	3.5
	1045.9 1044.2	45.8	20.2
	608.6 607.7	62.8	27.7
	432.4 424.5	227.0	100.0
835	1464.1 1460.1	10.3	3.3
	1045.7 1044.0	74.5	23.9
	610.0 608.0	71.5	22.9
	431.9 424.0	311.4	100.0

The progress of the photolysis was monitored by infrared spectroscopy, Figure 49 (Nicolet Interferometer)

	Line Position (Average)	Relative Intensity (Average)
A'	1464 1460	3.6
B'	1046 1044	20.3
C'	609 608	27.8
D'	432 425	100.0

d) Warm-up Diffusion Study.

The base temperature of the cryotip (7-8°K) was increased stepwise to the following temperatures: 15, 20, 25, 30 and 33°K. Then, the temperature was maintained at 33°K for about 30 min and finally increased to a maximum of 36°K.

The diffusion-controlled dimerization of cyclobutadiene-d_4 was monitored continuously by infrared spectroscopy.

Time	Reservoir Pressure (Torr)	Flow Rate (SCC/min, flow meter)	Line Pressure (Torr)	Cold Tip Temperature		Cryostat Pressure (Torr)
				Controller (Ω)	Readout (°K)	
11.50	39.9	2.0-2.2	2.7	100.00	16.4	2×10^{-8}
12.00	38.7	2.2	2.5	102.00	15.9	5×10^{-5}
12.15	37.5	2.0-2.4	2.2	102.00	15.9	5×10^{-5}
12.30	35.0	2.3-2.4	2.5	103.00	15.6	6×10^{-5}
12.50	33.1	2.0-2.4	2.4	104.00	15.4	6×10^{-5}
1.05	31.6	2.2	2.4	107.00	14.9	5×10^{-5}
1.25	29.2	2.2-2.4	2.5	109.00	14.7	2×10^{-5}
1.50	26.7	2.4	2.5	109.00	14.6	2×10^{-5}
2.15	23.8	2.2-2.5	2.5	109.00	14.6	5×10^{-6}
2.40	20.8	2.0-2.6	2.3	113.00	14.0	2×10^{-5}
2.50	19.8	2.4	2.5	113.00	13.9	2×10^{-5}

TABLE 14

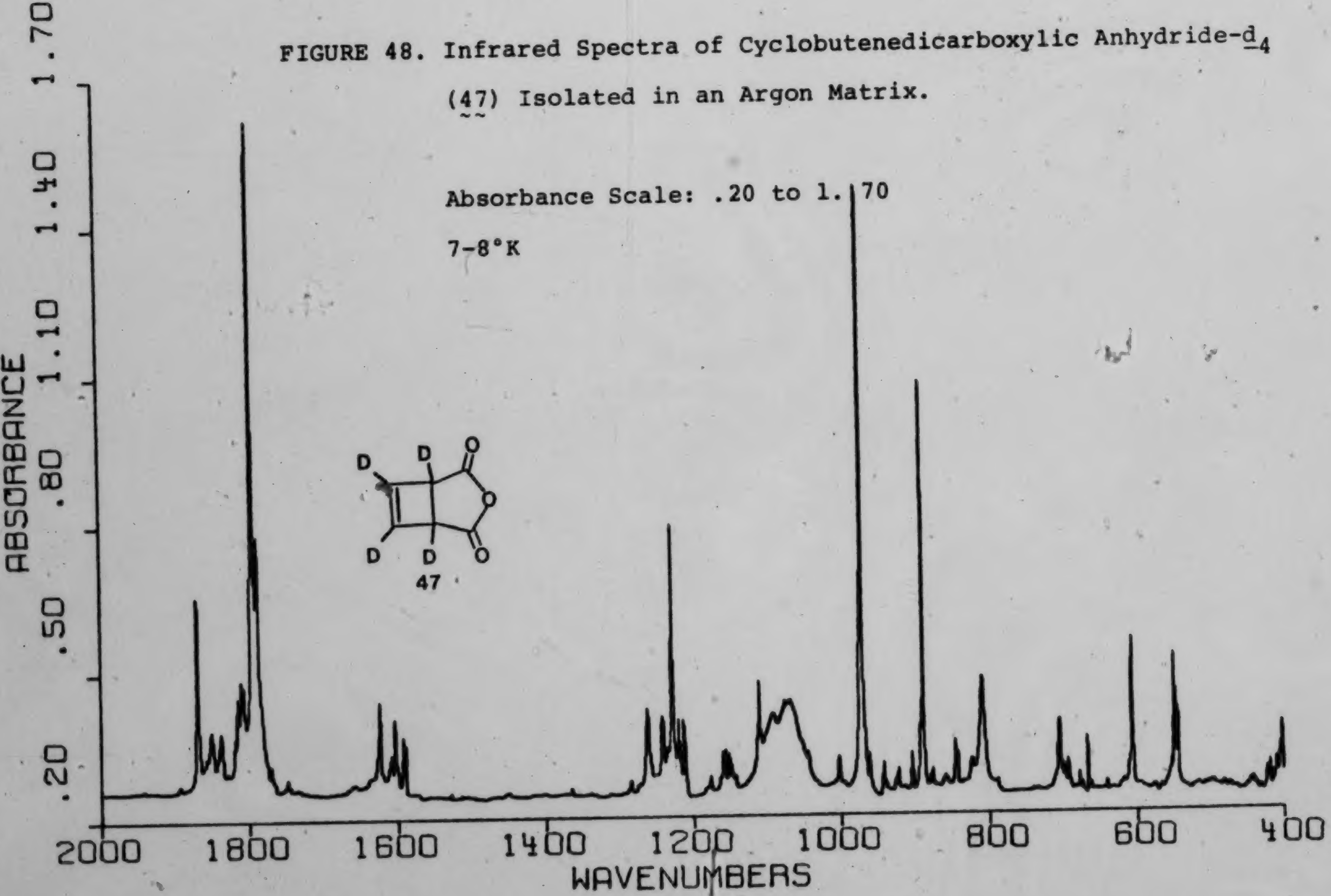
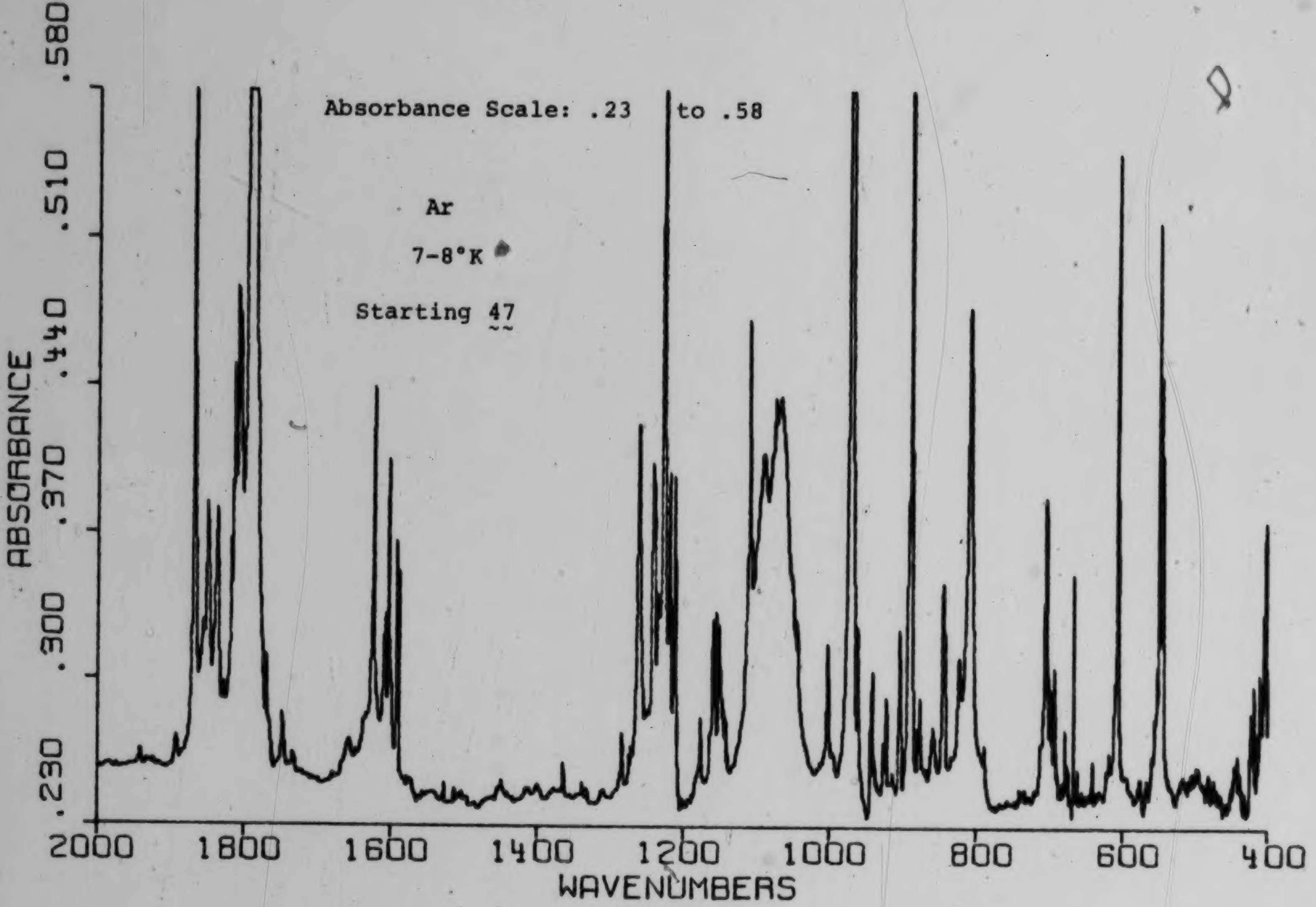


FIGURE 48. Infrared Spectra of Cyclobutenedicarboxylic Anhydride-$\underline{d}_4$ (47) Isolated in an Argon Matrix.

Absorbance Scale: .20 to 1.70

7-8°K


Absorbance Scale: .23 to .58
Ar
7-8°K
Starting 47
ABSORBANCE
.230
.300
.370
.440
.510
.580
2000
1800
1600
1400
1200
1000
800
600
400
WAVENUMBERS

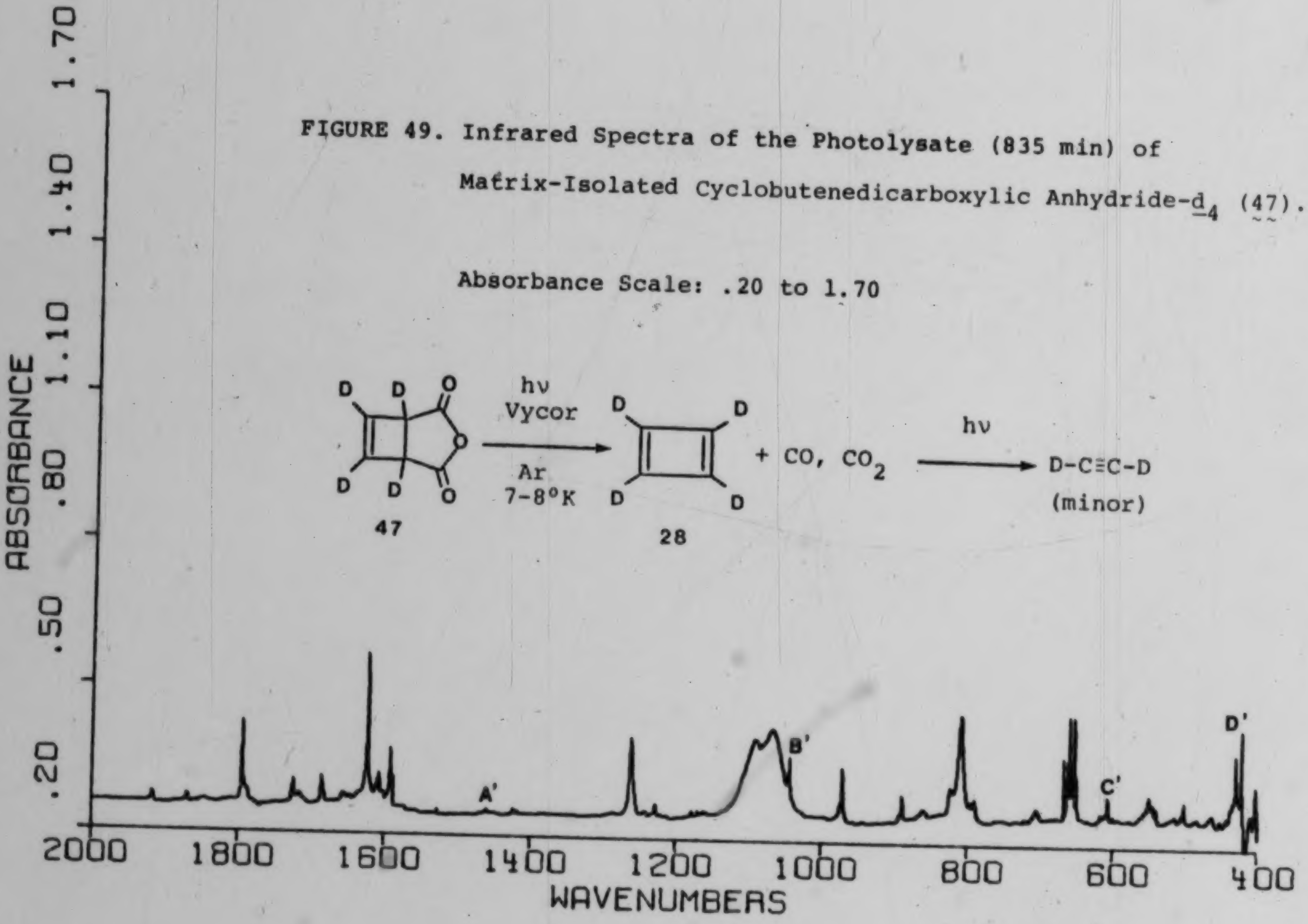
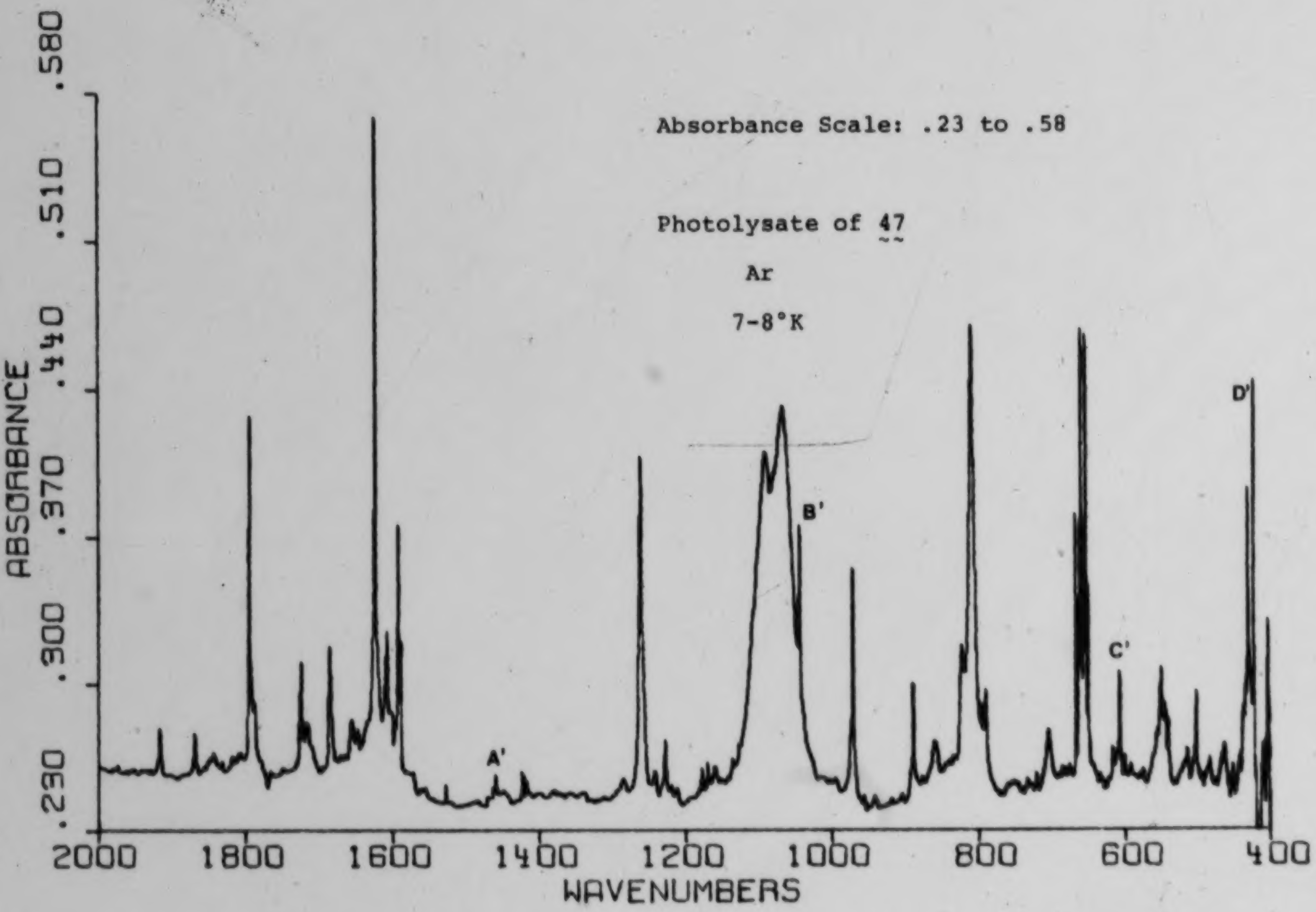


FIGURE 49. Infrared Spectra of the Photolysate (835 min) of Matrix-Isolated Cyclobutenedicarboxylic Anhydride-$\underline{d}_4$ (47).

Absorbance Scale: .20 to 1.70



Absorbance Scale: .23 to .58

Photolysate of 47

Ar

7-8°K

Cyclobutadiene-$\underline{h}_4$ ($\underset{\sim}{1}$) from Photo-α-pyrone-$\underline{h}_4$ ($\underset{\sim\sim}{18}$) Isolated in an Argon Matrix

Matrix-isolated photo-α-pyrone was prepared by irradiation of α-pyrone through Pyrex using two medium pressure mercury lamps. The resulting photolysate was converted into cyclobutadiene (main product) and acetylene (minor by-product) by irradiating through Vycor.

a) Cooling of the Target.

Pressure in the cryostat: 5 x 10^{-7} Torr

Temperature controller setting: 230.00 Ω, Germanium sensor

Heater: off

Cooling time: 90 min

Temperature read-out: 10°K (potentiometer)

b) Deposition of the Matrix-Precursor Mixture.

Substrate temperature : "finger", 0-5°C (ice-water bath) line, room temperature

c) Photolysis of Matrix-Isolated α-Pyrone.

Lamps: two medium pressure mercury vapor

Filters: Pyrex

Irradiation time: 18 h (Figure 51)

d) Photolysis of Matrix-Isolated Photo-α-pyrone.

Lamps: two medium pressure mercury vapor

Filters: Vycor

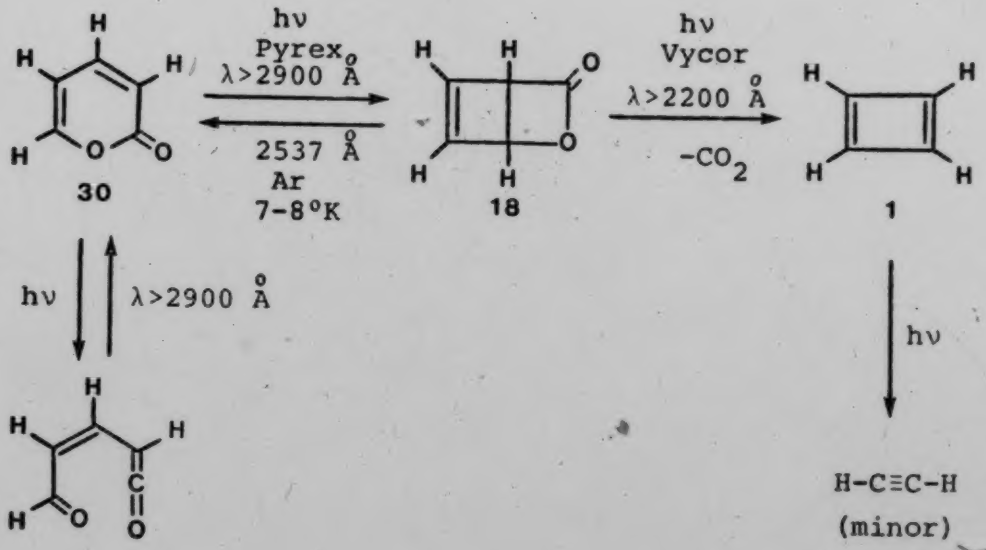
The generation of cyclobutadiene was monitored with the Nicolet Interferometer (Figure 52)

Irradiation Time (min)	Line Position (cm^{-1})	Integrated Absorbance (cm^{-1}) x 10^3	Relative Intensity
90	1531.6 1529.5	4.0	1.3
	1243.7 1241.0	100.3	32.0
	721.7 719.5	21.5	6.8
	576.0 574.4	313.1	100.0
270	1530.4 1529.2	6.0	1.5
	1243.6 1241.2	149.6	38.1
	721.3 719.5	26.0	6.6
	576.1 574.4	392.0	100.0
420	1530.9 1529.4	6.5	1.4
	1243.8 1241.2	162.1	35.0
	720.8 719.2	32.4	7.0
	576.0 574.5	463.3	100.0

	Line Position (Average)	Relative Intensity (Average)
A	1531 1529	1.4
B	1244 1241	35.0
C	721 719	6.8
D	576 574	100.0

e) Warm-up Diffusion Study.

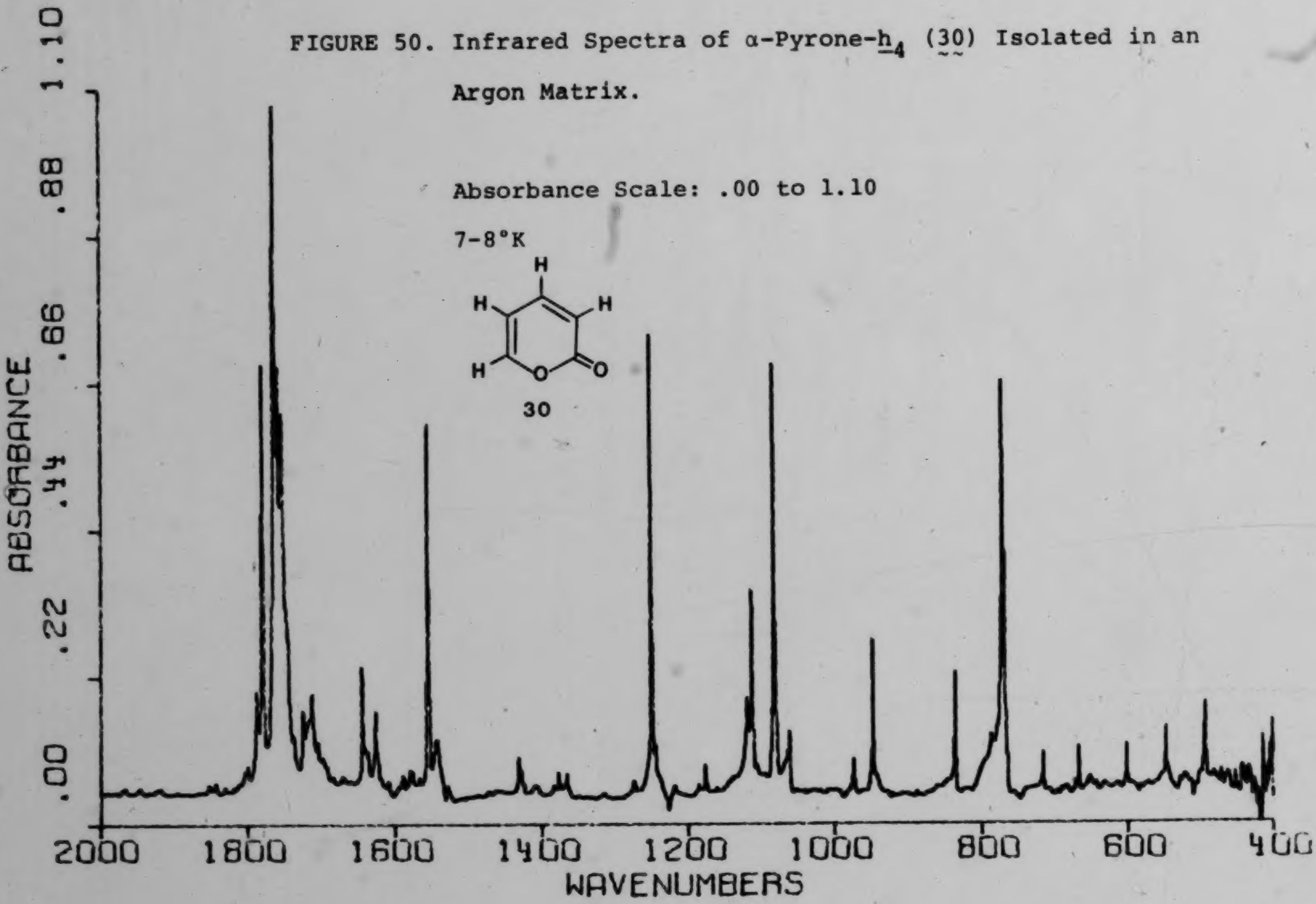
The temperature of the matrix was gradually increased to 35°K while the effects of this warming were monitored by infrared spectroscopy (Nicolet Interferometer).


hν
Pyrex
λ>2900 Å
2537 Å
Ar
7-8°K
hν
Vycor
λ>2200 Å
$-CO_2$
hν
λ>2900 Å
hν
30
18
1
H-C≡C-H
(minor)

Time	Reservoir Pressure (Torr)	Flow Rate (SCC/min, flow meter)	Line Pressure (Torr)	Cold Tip Temperature		Cryostat Pressure (Torr)
				Controller (Ω)	Readout (°K)	
12.45	29.9	2.6	3.0	230.00	10-15	2×10^{-8}
1.00	28.4	2.5	2.5	"	"	5×10^{-7}
1.20	25.8	2.5-2.6	2.8	"	"	5×10^{-6}
1.30	24.0	2.6	3.0	"	"	2×10^{-5}
2.00	21.0	2.5-2.6	3.0	"	"	5×10^{-5}
2.15	19.0	2.3-2.6	3.0	"	"	5×10^{-5}

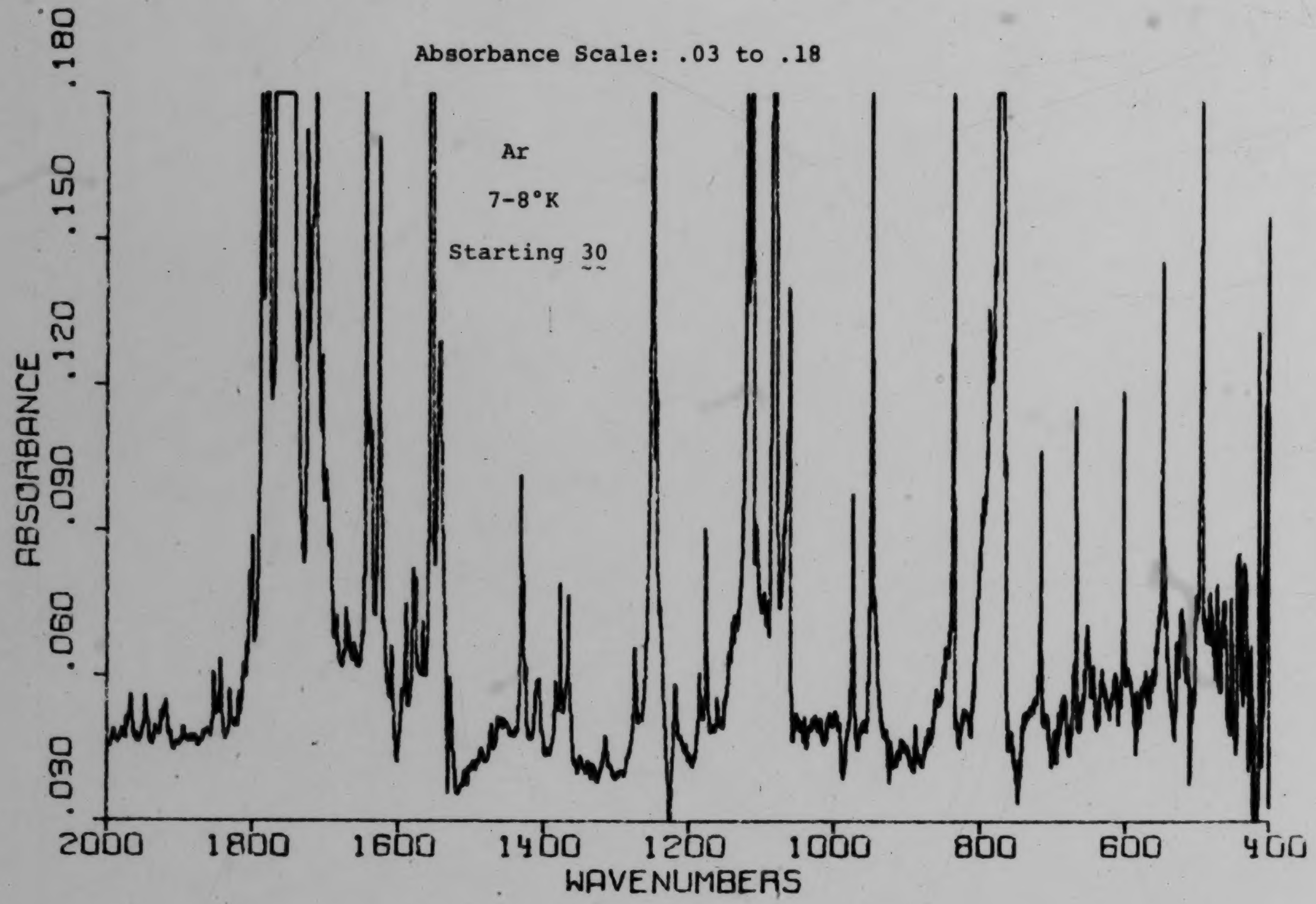
TABLE 15

FIGURE 50. Infrared Spectra of α-Pyrone-$\underline{h}_4$ (30) Isolated in an Argon Matrix.



Absorbance Scale: .00 to 1.10

7-8°K



Absorbance Scale: .03 to .18

Ar

7-8°K

Starting **30**

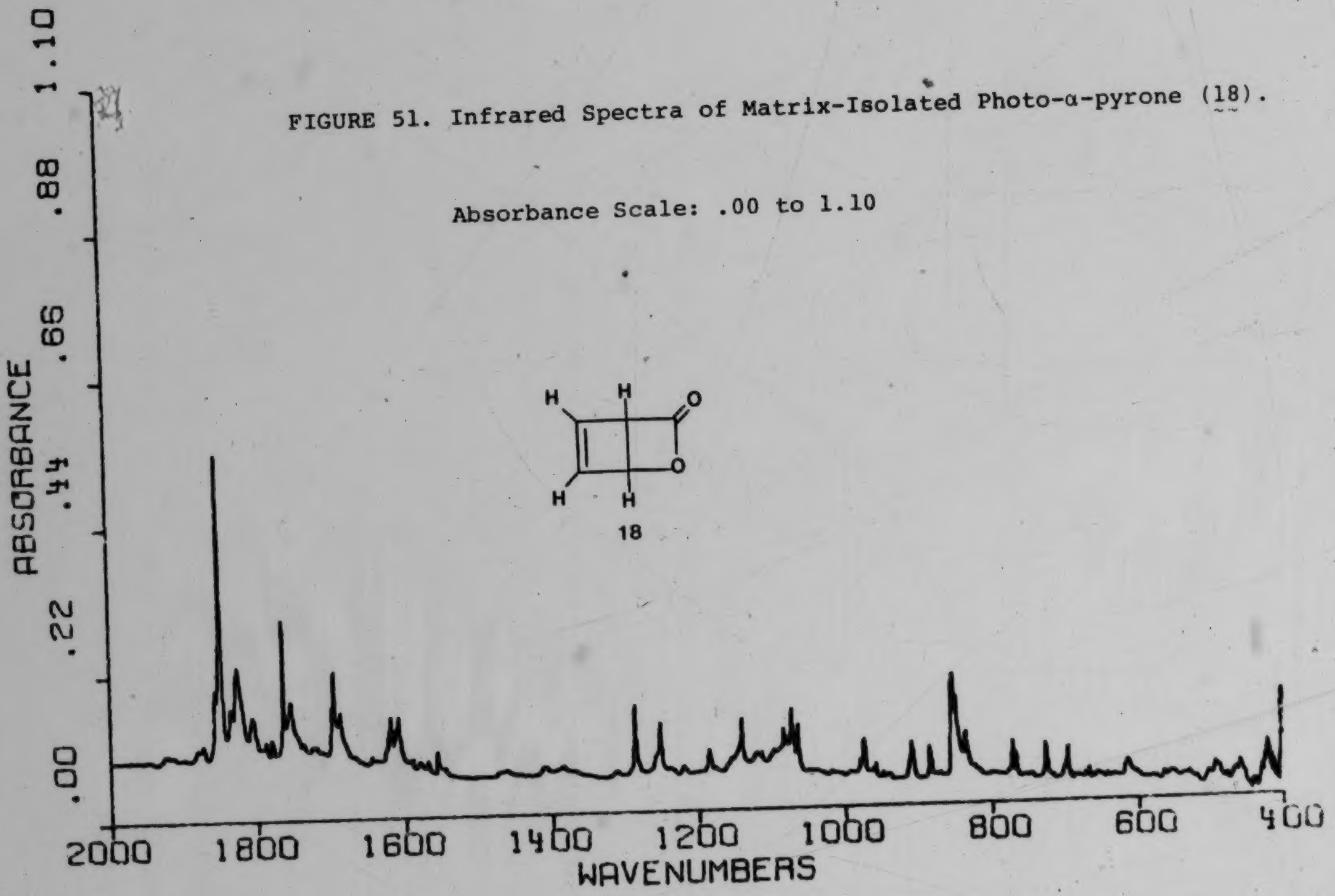


FIGURE 51. Infrared Spectra of Matrix-Isolated Photo-α-pyrone (18).

Absorbance Scale: .00 to 1.10

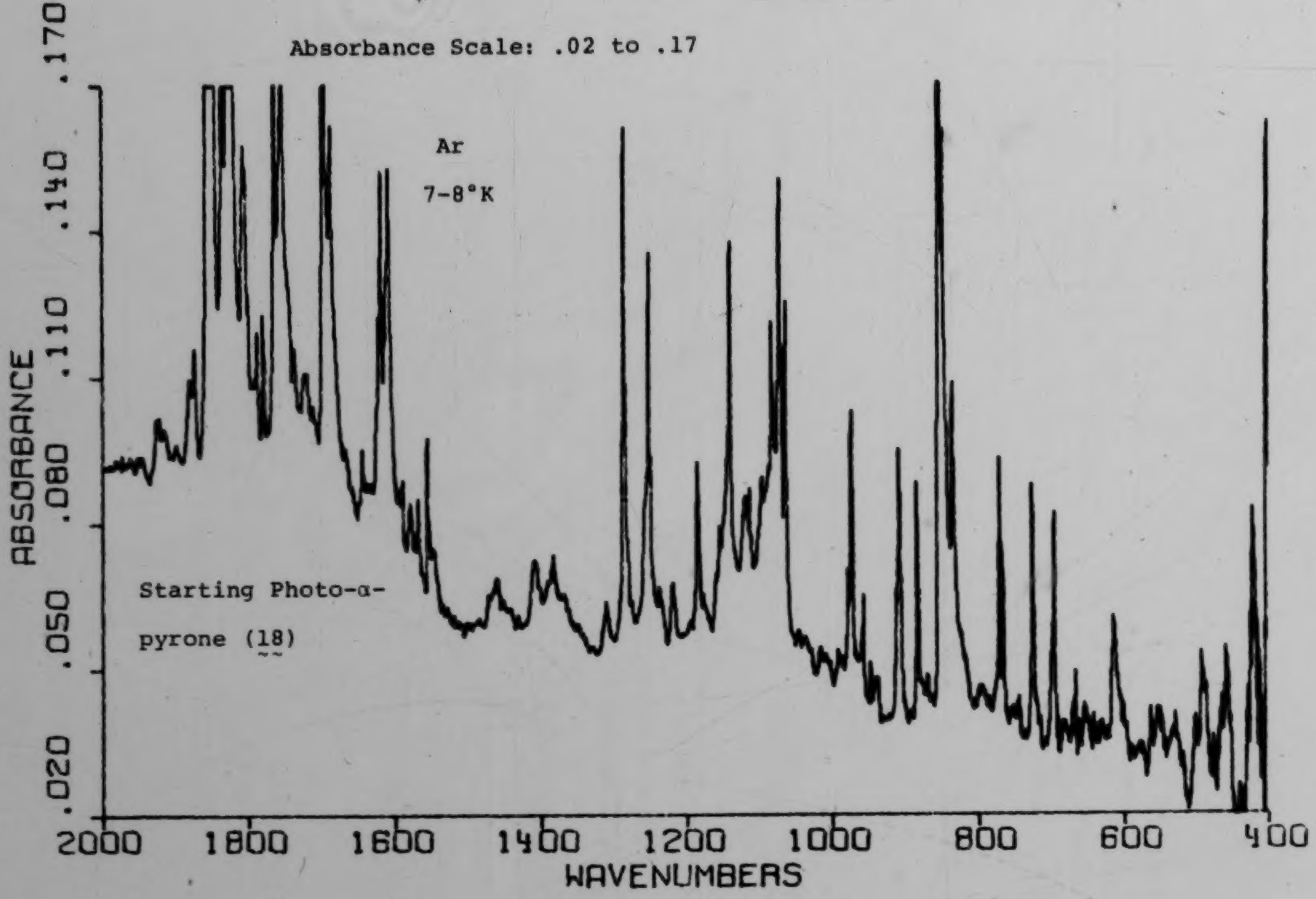
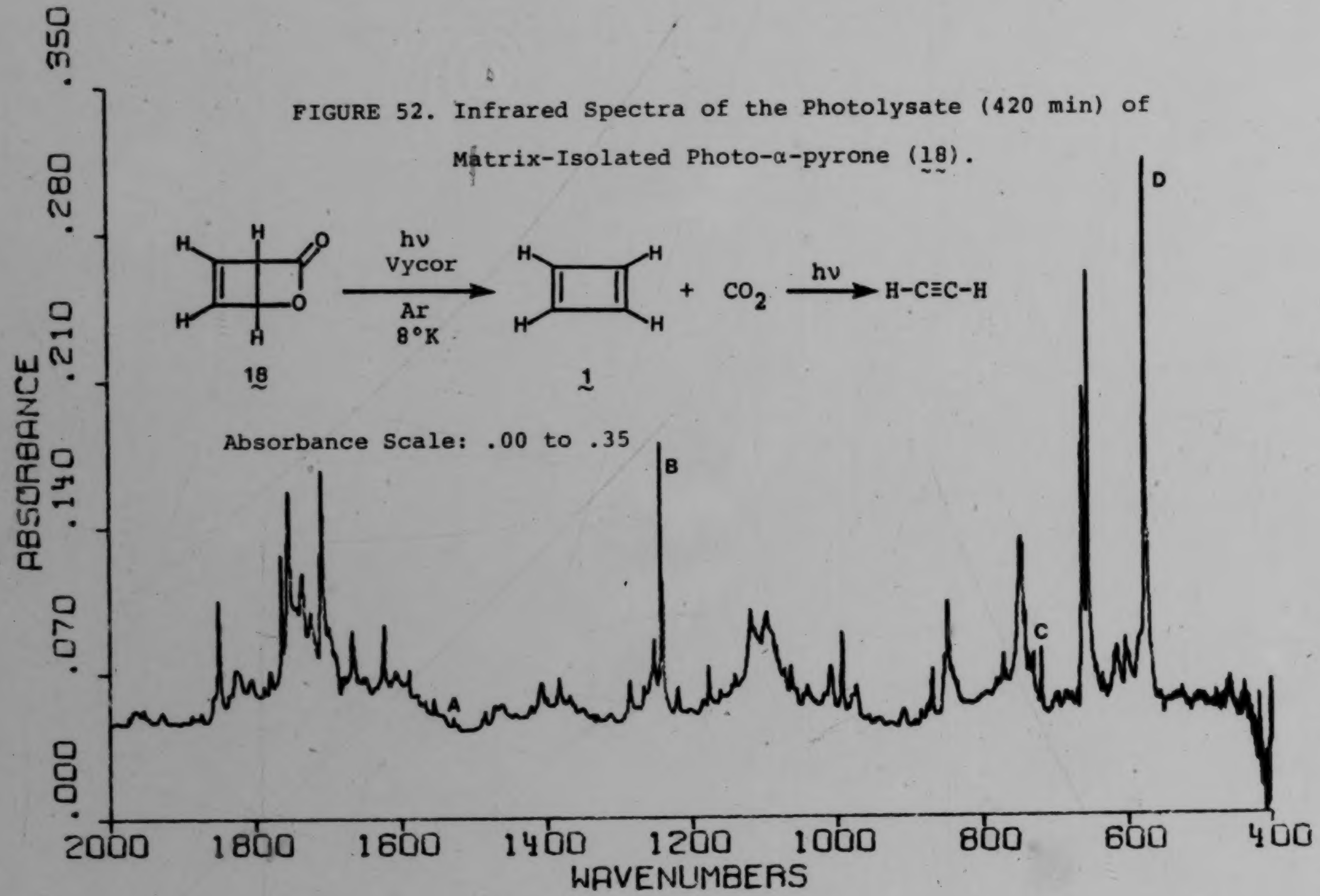
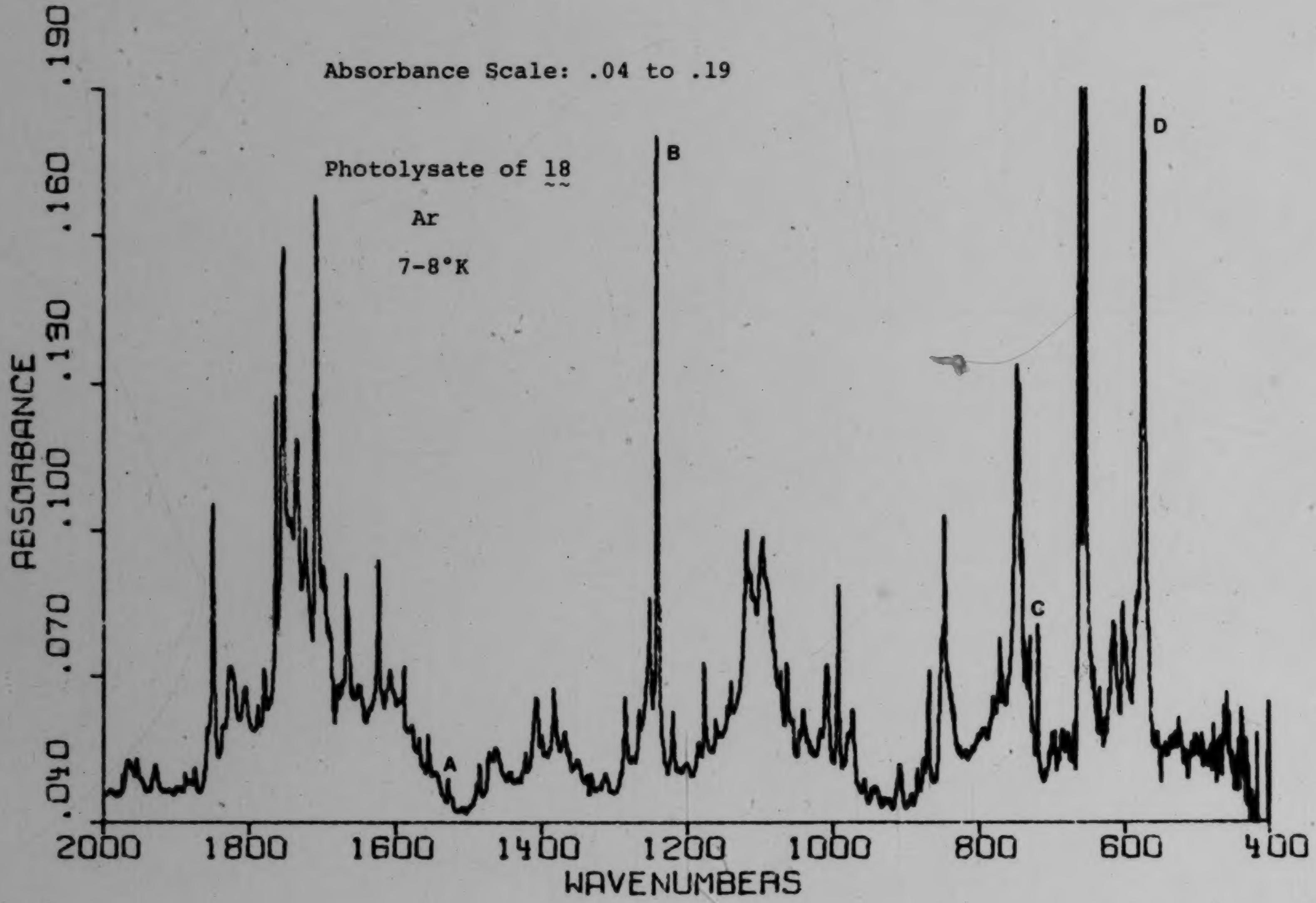

Absorbance Scale: .02 to .17
Ar
7-8°K
Starting Photo-α-pyrone (18)
ABSORBANCE
.020
.050
.080
.110
.140
.170
2000
1800
1600
1400
1200
1000
800
600
400
WAVENUMBERS

FIGURE 52. Infrared Spectra of the Photolysate (420 min) of Matrix-Isolated Photo-α-pyrone (18).





Absorbance Scale: .04 to .19

Photolysate of 18

Ar

7-8°K

Cyclobutadiene-$\underline{d}_4$ (28) from Photo-α-pyrone-$\underline{d}_4$ (48) Isolated in an Argon Matrix

Photo-α-pyrone-$\underline{d}_4$ was prepared in an argon matrix by irradiation through Pyrex of matrix-isolated α-pyrone-$\underline{d}_4$ using two medium pressure mercury lamps. The resulting photolysate was further irradiated through Quartz using low pressure mercury lamps.

a) Cooling of the Target.

Vacuum in cryostat: 2×10^{-4} Torr
Temperature controller and heater: off
Cooling time: 90 min
Temperature read-out: 13.0°K (digital indicator)

b) Deposition of the Matrix-Precursor Mixture.

Substrate and line at room temperature
Deposited: 27 Torr of Argon in 60 min (Table 16, Figure 53)

c) Photolysis of the Matrix-Isolated α-Pyrone-$\underline{d}_4$.

Lamps: two medium pressure mercury vapor
Filters: Pyrex
Irradiation time: 17 h (Figure 54)

d) Photolysis of the Matrix-Isolated Photo-α-pyrone-$\underline{d}_4$.

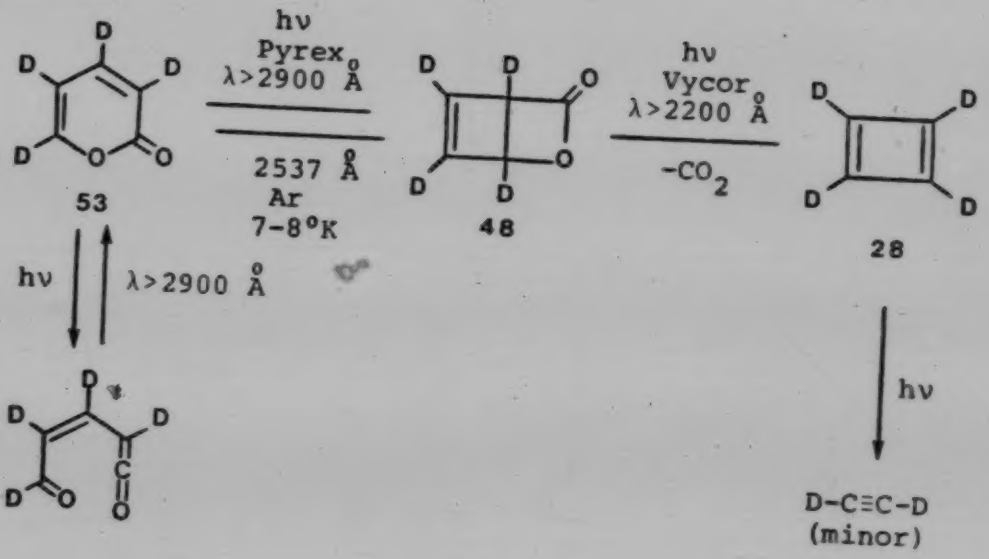
Lamps: two low pressure mercury vapor
Filters: Vycor
The progress of the photolysis was monitored by infrared spectroscopy, Figure 55 (Nicolet Interferometer)

Irradiation Time (min)	Line Position (cm^{-1})	Integrated Absorbance (cm^{-1}) x 10^3	Relative Intensity
130	1455.0 1450.1	5.6	2.5
	1047.2 1044.1	44.3	19.7
	609.3 608.4	46.3	20.6
	426.2 423.3	225.0	100.0
220	1455.4 1450.3	8.3	2.5
	1047.1 1044.3	79.6	23.9
	609.2 608.1	67.3	20.2
	426.4 423.2	333.4	100.0
280	1455.2 1450.4	10.0	2.5
	1047.2 1044.1	88.3	21.8
	609.3 608.0	82.4	20.4
	426.3 423.4	404.2	100.0

	Line Position (Average)	Relative Intensity (Average)
A'	1455 1450	2.5
B'	1047 1044	21.8
C'	609 608	20.4
D'	426 423	100.0

e) Warm-up Diffusion Study.

The temperature of the matrix was gradually increased to a maximum of 35°K, then was maintained at 35°K until no further change could be observed in the infrared spectra.


hν
Pyrex
λ>2900 Å
2537 Å
Ar
7-8°K
hν
Vycor
λ>2200 Å
-CO2
hν
λ>2900 Å
hν
53
48
28
D-C≡C-D
(minor)

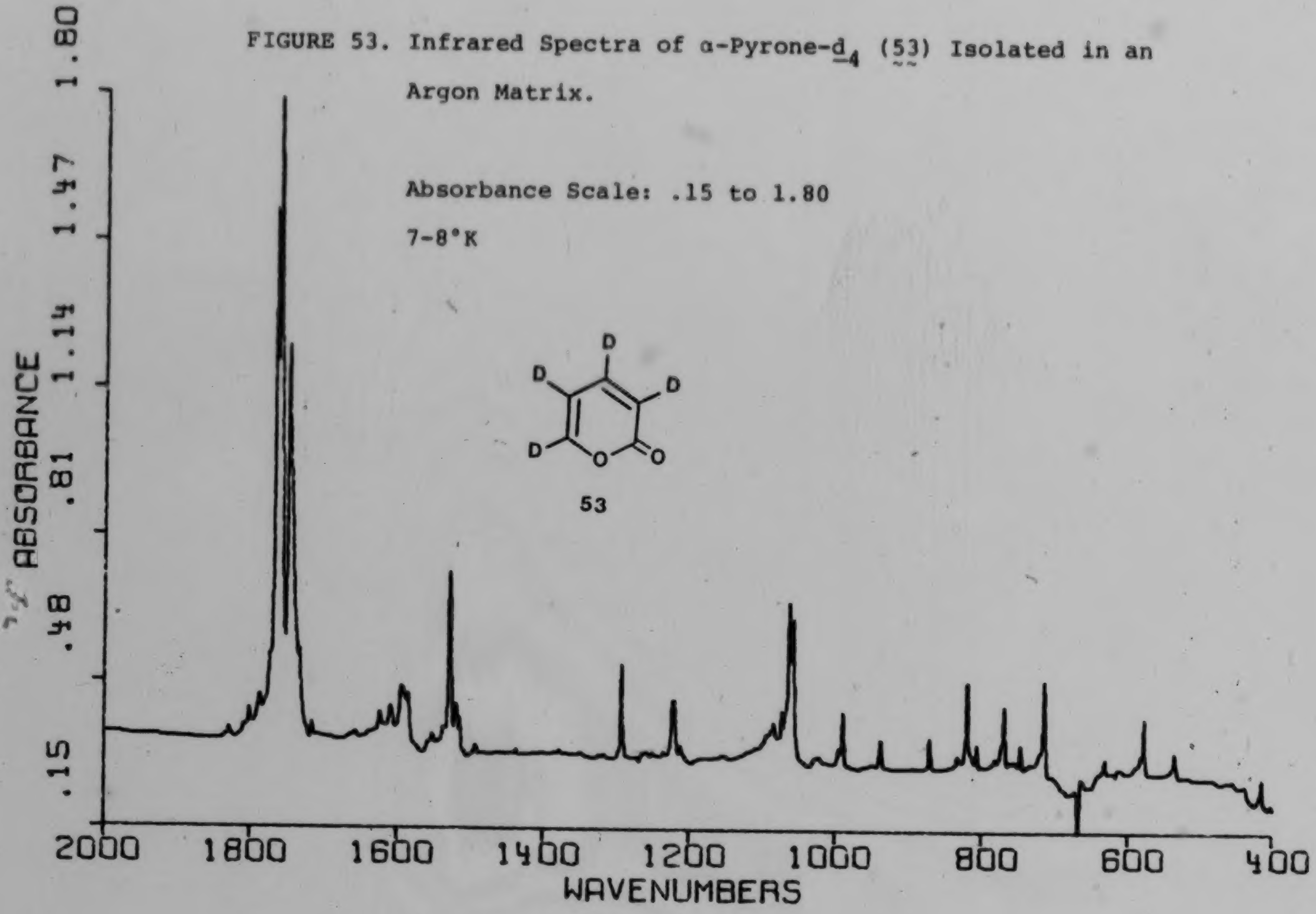
Time	Reservoir Pressure	Flow Rate	Line Pressure	Cold Tip Temperature		Cryostat Pressure
				Controller	Readout	
	(Torr)	(SCC/min, flow meter)	(Torr)	(Ω)	(°K)	(Torr)
11.00	72	1.8	2.5	-	-	5×10^{-6}
12.00	45	1.8	3.0	-	-	5×10^{-4}

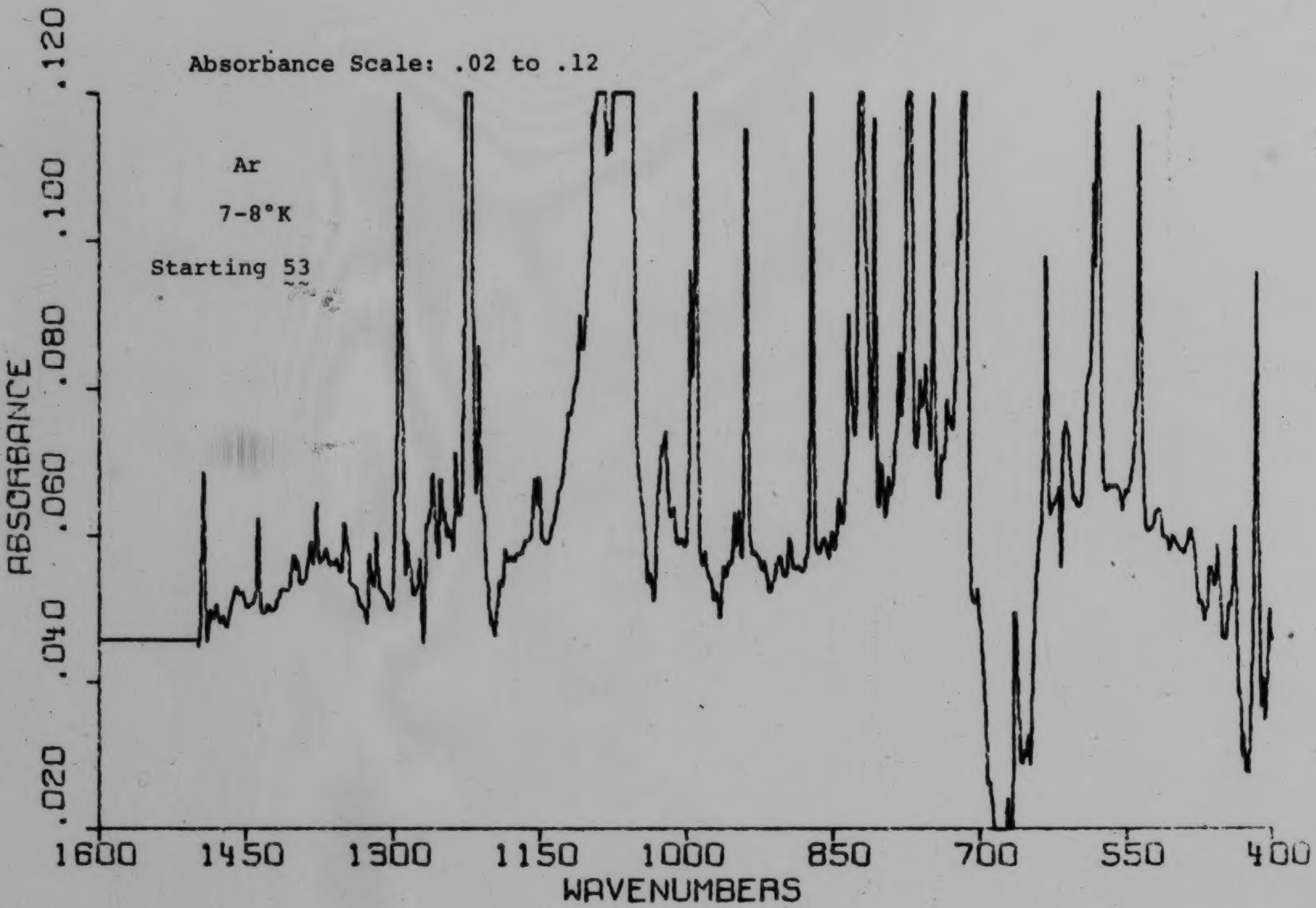
TABLE 16

FIGURE 53. Infrared Spectra of α-Pyrone-$\underline{d}_4$ (53) Isolated in an Argon Matrix.

Absorbance Scale: .15 to 1.80

7-8°K





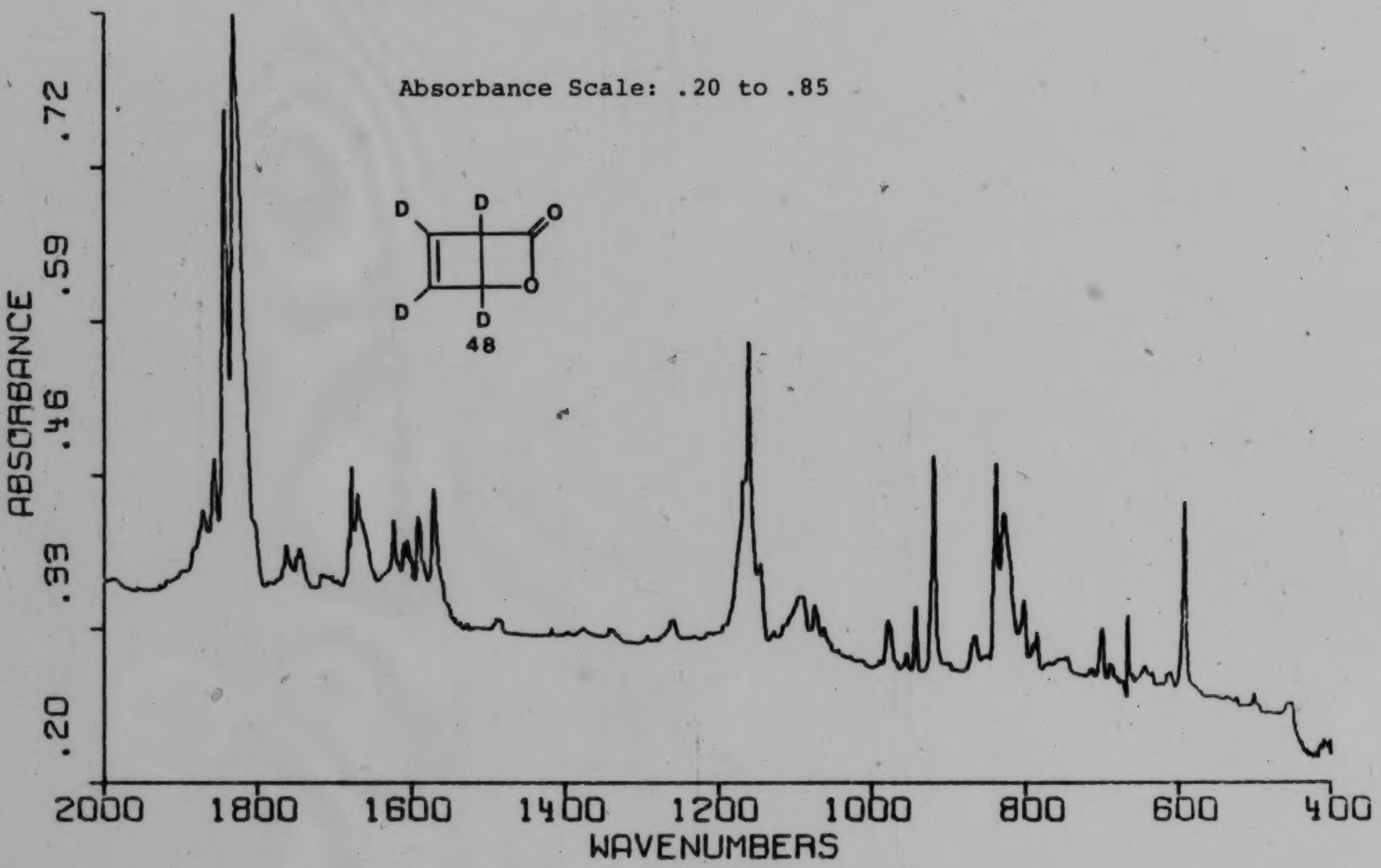
Absorbance Scale: .02 to .12

Ar

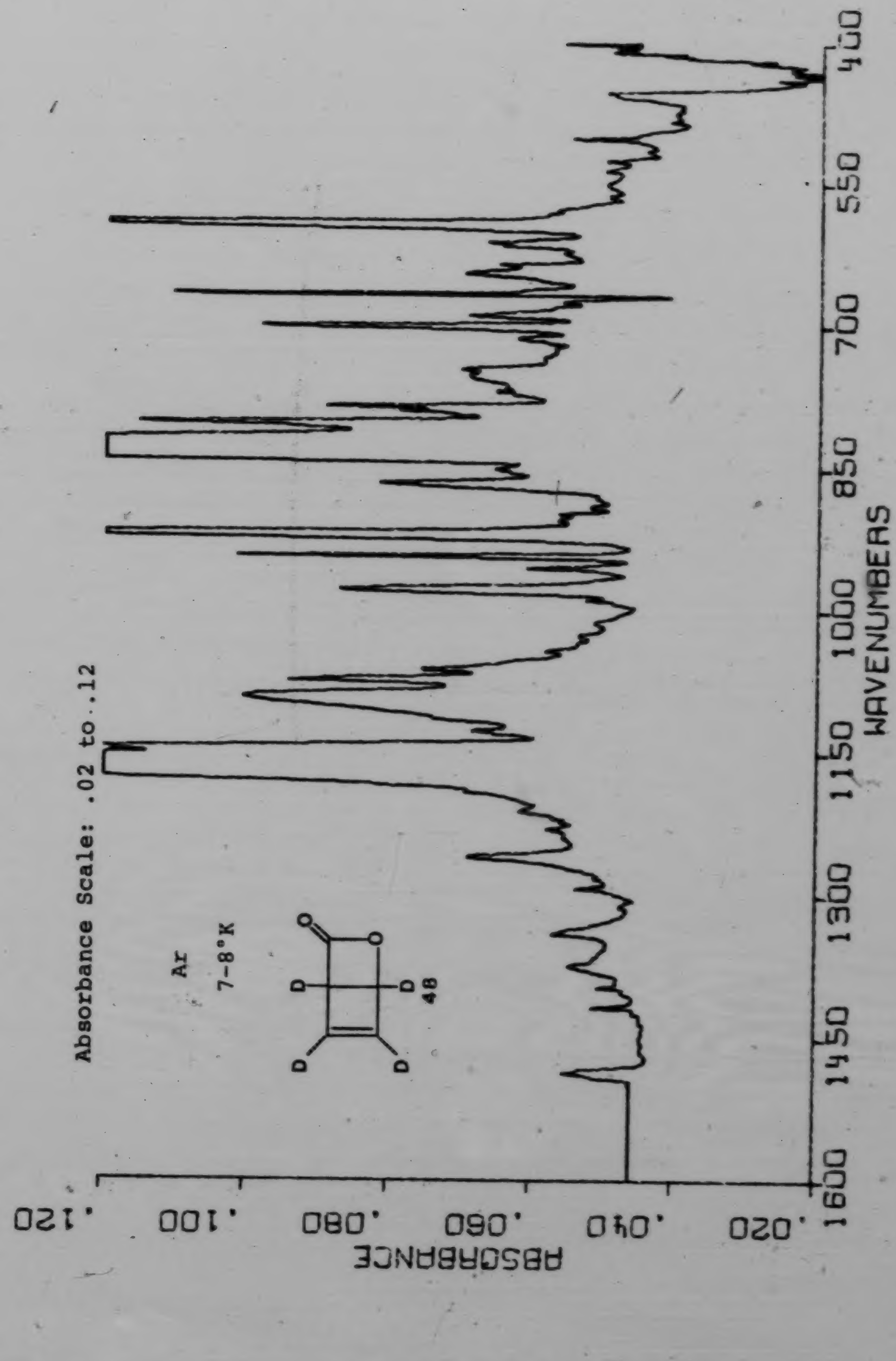
7-8°K

Starting 53

FIGURE 54. Infrared Spectra of Matrix-Isolated Photo-α-pyrone-$\underline{d}_4$ (48).



Absorbance Scale: .20 to .85


Absorbance Scale: .02 to .12
Ar
7-8°K
D
D
D
D
ABSORBANCE
.020
.040
.060
.080
.100
.120
WAVENUMBERS
1600
1450
1300
1150
1000
850
700
550
400

48

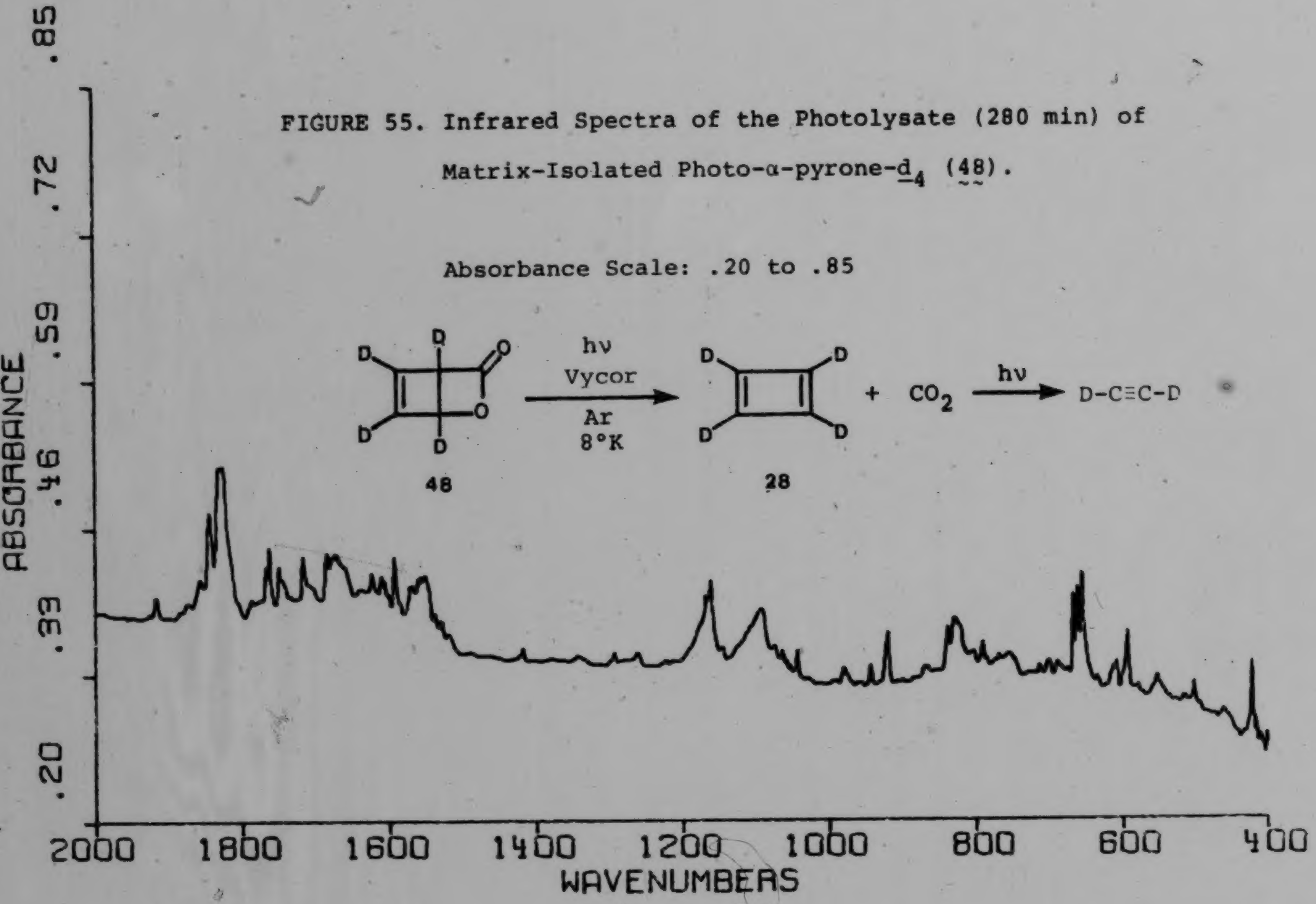
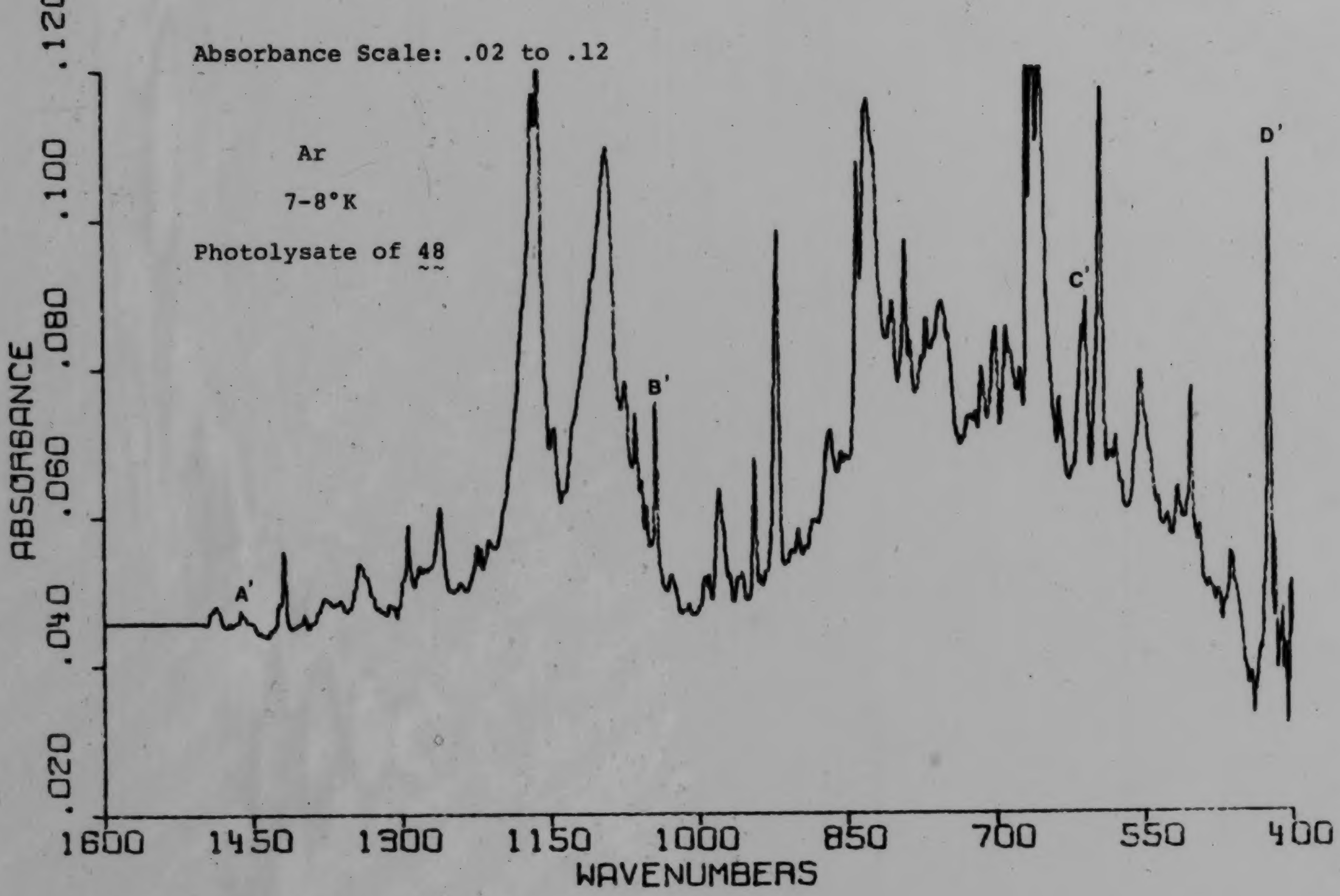


FIGURE 55. Infrared Spectra of the Photolysate (280 min) of Matrix-Isolated Photo-α-pyrone-$\underline{d}_4$ (48).

Absorbance Scale: .20 to .85


Absorbance Scale: .02 to .12
Ar
7-8°K
Photolysate of 48
A'
B'
C'
D'
ABSORBANCE
.020
.040
.060
.080
.100
.120
WAVENUMBERS
1600
1450
1300
1150
1000
850
700
550
400

Cyclobutadiene Dimer-h_8 (**29**) in an Argon Matrix

a) Cooling of the Target.

Pressure in the cryostat: 2 x 10^{-7} Torr

Temperature controller setting: 200.00 Ω,
Germanium sensor

Heater: 4%

Cooling time: 60 min

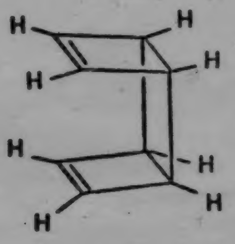
Temperature read-out: 10-13°K (potentiometer)

The twice degassed dimer **29** (400 mTorr), was vacuum transferred into the mixing bulb and diluted with about 30 Torr of dry argon. The mixture had an equilibrium pressure of 31.6 Torr.

b) Deposition of the Guest-Host Mixture.

Deposited: 15.2 Torr of mixture in 140 min (Table 17)

ir (Ar, 7-8°K) cm^{-1}: 3110 (w), 3040 (m), 2900 (s), 1545 (w), 1290 (s), 1179 (m), 1155 (m), 1000 (w), 960 (m), 820 (m), 795 (s), 750 (m), 740 (m), 450 (m), 420 (w)



29

Time	Reservoir Pressure	Flow Rate	Line Pressure	Cold Tip Temperature		Cryostat Pressure
				Controller	Readout	
	(Torr)	(SCC/min, flow meter)	(Torr)	(Ω)	(°K)	(Torr)
2.10	3.16	2.1-2.2	3.0	200.00	10-13	2×10^{-5}
3.10	25.1	1.9-2.3	3.1	"	"	5×10^{-5}
4.15	18.1	2.0-2.3	3.5	"	"	2×10^{-5}
4.30	16.4	2.1-2.4	3.5	"	"	2×10^{-5}

TABLE 17

Cyclobutadiene Dimer-$\underline{d}_8$ ($\underset{\sim\sim}{45}$) Isolated in an Argon Matrix

a) Cooling of the Target.

Pressure in the cryostat: 2×10^{-6} Torr

Temperature controller setting: 225.50 Ω,
Germanium sensor

Heater: off

Cooling time: 105 min

Temperature read-out: 10°K (potentiometer)

The dimer $\underset{\sim\sim}{45}$ was degassed three times and vacuum transferred into the mixing bulb to give a pressure of 500 mTorr at room temperature. About 30 Torr of dry argon were added. Upon mixing and equilibration at room temperature the mixture had a pressure of 33.4 Torr.

b) Deposition of the Guest-Host Mixture.

Deposited: 7.5 Torr of mixture in 60 min (Table 18, Figure 56).

Acetylene-$\underline{h}_2$ Isolated in an Argon Matrix

a) Cooling of the Target

Pressure in the cryostat: 2×10^{-7} Torr

Temperature controller setting: 210.00 Ω,
Germanium sensor

Heater: off

Time	Reservoir Pressure	Flow Rate	Line Pressure	Cold Tip Temperature		Cryostat Pressure
				Controller	Readout	
	(Torr)	(SCC/min, flow meter)	(Torr)	(Ω)	(°K)	(Torr)
1.15	33.4	2.5	0	225.50	10	2×10^{-8}
1.40	30.6	2.3	2.8	"	"	5×10^{-7}
2.15	25.9	2.3	3.0	"	"	1×10^{-6}

TABLE 18

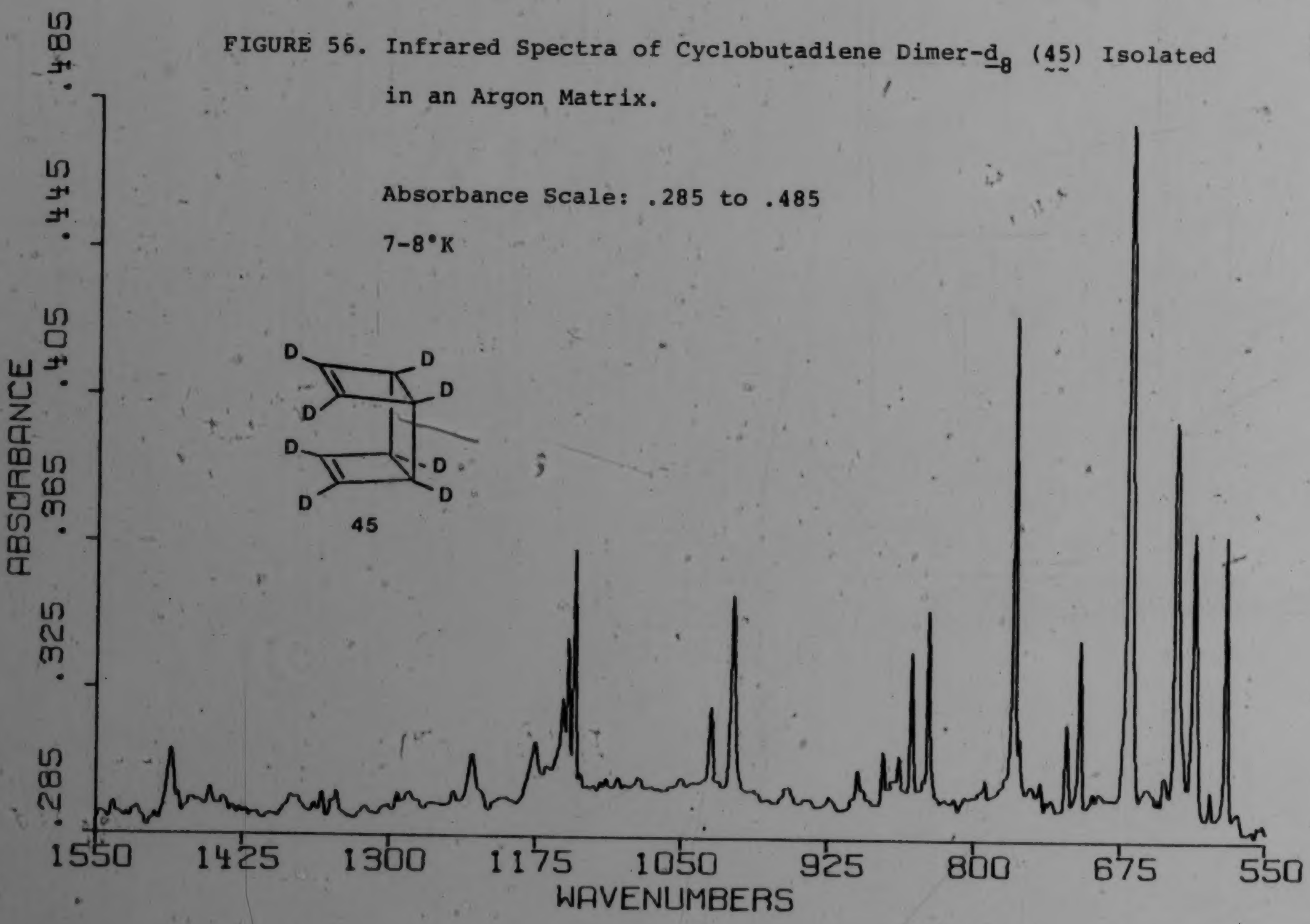
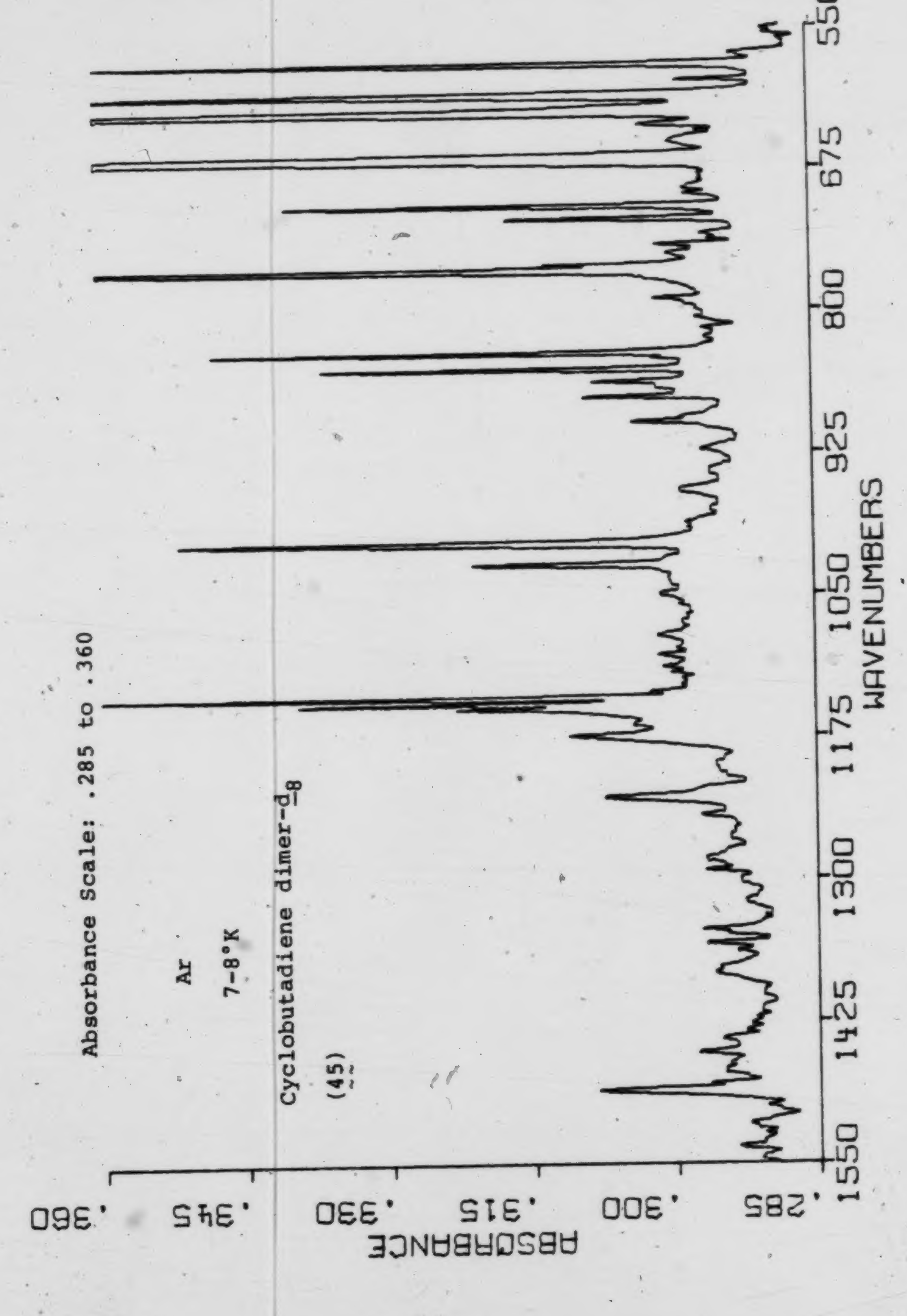


FIGURE 56. Infrared Spectra of Cyclobutadiene Dimer-$\underline{d}_8$ (45) Isolated in an Argon Matrix.

Absorbance Scale: .285 to .485

7-8°K

45


Absorbance Scale: .285 to .360
Ar
7-8°K
Cyclobutadiene dimer-d_8
(45)
ABSORBANCE
.285
.300
.315
.330
.345
.360
WAVENUMBERS
1550
1425
1300
1175
1050
925
800
675
550

Cooling time: 90 min

Temperature read-out: 10-13°K (potentiometer)

Acetylene (100 Torr) was vacuum transferred through a dry ice-acetone trap into a 30 ml reservoir having a teflon isolating valve. The gas was frozen (liquid N_2) to give a colorless solid which was degassed twice and then sublimed into the mixing bulb. An equilibration pressure of 500 mTorr was obtained at room temperature. About 42 Torr of dry Argon were passed into the reservoir so that the mixture had a pressure of 44.7 Torr at room temperature.

b) Deposition of the Guest-Host Mixture.

Deposited: 12 Torr of mixture in 95 min (Table 19)

ir (Ar, 7-8°K cm^{-1}: 3240 (s), 1395 (w), 765 (vs)

Time	Reservoir Pressure (Torr)	Flow Rate (SCC/min, flow meter)	Line Pressure (Torr)	Cold Tip Temperature Controller (Ω)	 Readout (°K)	Cryostat Pressure (Torr)
2.10	44.7	2.0-2.5	0	210.00	10-13	2×10^{-8}
2.45	41.2	2.2-2.5	3.1	"	"	2×10^{-5}
2.55	40.4	2.4	3.9	"	"	2×10^{-5}
3.45	32.7	2.3-2.5	3.9	"	"	2×10^{-5}

TABLE 19

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'Colegio del Sacromonte'
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Higher Certificate, 'A' level, June 1967
1960-67

Matriculation
The University of Granada
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1967-68

Higher Education

Licentiate of Science Degree
University of Granada
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Specialization in Physical, Analytical and Organic Chemistry
Final Oral Examination in Lic. Sc. at the University of Granada with First Class Mark, June 1973.
1968-73

Licentiate of Science with Special Distinction
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RESEARCH EXPERIENCE

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1. Synthesis and characterization of strained hydrocarbon rings.

2. Development of new reagents and improvement of existing synthetic methods to effect organic transformations under mild reaction conditions with direct application in the Chemistry of Natural Products.

   Dehydration of alcohols via alkoxy phosphonium salts, in connection with the syntheses of the hydrocarbon 1,5-methano[10]annulene and the macrolide antibiotic Cytochalasin B.

   Carbon-carbon bond formation by the utilization of α-stabilized carbanions.

   Synthesis and reactivity of 2-benzothiazolyl thiol esters. Intermolecular ester formation and applicability to lactone formation in connection with the total synthesis of the macrolide antibiotic Cytochalasin B.

Hydrolysis of esters in synthetically interesting environments in connection with the total synthesis of the macrolide antibiotics.

2-Chloro-N-methylbenzothiazolium trifluoromethanesulphonate: A useful condensing agent for the formation of esters, thiol esters and amides.

Chemistry of the alkoxy immonium salts. Nucleophilic attack on 2-alkoxy-N-methylbenzothiazolium salts: formation of esters, phenoxyethers and thioethers, quaternary ammonium and phosphonium salts and alkyl halides.

3. Low Temperature Spectroscopy.

   Matrix Isolation Technique.

   Photochemistry in rare gas matrices (photochemical generation of unstable species).

PROFESSIONAL AFFILIATIONS: American Chemical Society.

RESEARCH INTERESTS

Development of new reagents.

Synthesis of natural products (antibiotics, antitumor agents and compounds with potential biochemical activity).

Study of theoretically interesting molecules (elucidation of the nature of the bonding in organic molecules).

AWARDS AND SCHOLARSHIPS

Board of Equal Opportunities Scholarship
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Prize in the contest on Energy with the essay:
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Sponsored by "Compañia Sevillana de Electricidad" in
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University of Granada
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Province of Madrid Fellowship
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PUBLICATIONS

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